Thermodynamics

Henri J.F. Jansen
Department of Physics
Oregon State University

December 14, 2003

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Introduction.

Thermodynamics??? Why? What? How? When? Where? Many questions to ask, so we will start with the first one. A frequent argument against studying thermodynamics is that we do not have to do this, since everything follows from statistical mechanics. In principle, this is, of course, true. This argument, however, assumes that we know the exact description of a system on the microscopic scale, and that we can calculate the partition function. In practice, we can only calculate the partition function for a few simple cases, and in all other cases we need to make serious approximations. This is where thermodynamics plays an invaluable role. In thermodynamics we derive basic equations that all systems have to obey, and we derive these equations from a few basic principles. In this sense thermodynamics is a meta-theory, a theory of theories, very similar to a study of non-linear dynamics. Thermodynamics gives a framework for the results derived in statistical mechanics, and allows us to check if approximations made in statistical mechanical calculations violate some of these basic results. For example, if the calculated heat capacity in statistical mechanics is negative, we know we have a problem!

Thermodynamics also gives us a language for the description of experimental results. It defines observable quantities, especially in the form of response functions. It gives the definitions of critical exponents and transport properties. It allows analyzing experimental data in the framework of simple models, like equations of state. It provides a framework to organize experimental data. To say that we do not need this is quite arrogant, and assumes that if you cannot follow the (often very complicated) derivations in statistical mechanics you might as well give up. Thermodynamics is the meeting ground of experimenters and theorists. It gives the common language needed to connect experimental data and theoretical results.

Classical mechanics has its limits of validity, and we need relativity and/or quantum mechanics to extend the domain of this theory. Thermodynamics and statistical mechanics do not have such a relation, though, contrary to what people claim who believe that we do not need thermodynamics. A prime example is the concept of entropy. Entropy is defined as a measurable quantity in thermodynamics, and the definition relies both on the thermodynamic limit (a large system) and the existence of reservoirs (an even larger outside). We can also define entropy in statistical mechanics, but purists will only call this an entropy analogue. It is a good one, though, and it reproduces many of the well known results. The statistical mechanical definition of entropy can also be applied to very small systems, and to the whole universe. But problems arise if we now also want to apply the second law of thermodynamics in these cases. Small system obey equations which are symmetric under time reversal, which contradicts the second law. Watch out for Maxwell's demons! On the large scale, the entropy of the universe is probably increasing (it is a very large system, and

by definition isolated). But if the universe is in a well defined quantum state, the entropy is and remains zero! These are very interesting questions, but for a different course. Confusing paradoxes arise easily if one does not appreciate that thermodynamics is really a meta-theory, and when one applies concepts under wrong conditions.

And what if you disagree with what was said above? Keep reading nevertheless, because thermodynamics is also fun. Well, at least for me it is......

The material in front of you is not a textbook, nor is it an attempt at a future textbook. There are many excellent textbooks on thermodynamics, and it is not very useful to add a new textbook of lower quality. Also, when you write a textbook you have to dot all the t-s and cross all the i-s, or something like that. You get it, I am too lazy for that. This set of notes is meant to be a tool to help you study the topic of thermodynamics. I have over the years collected the topics I found relevant, and working through these notes will give you a good basic understanding of what is needed in general. If any important topic is missing, I would like to know so I can add it. If you find a topic too far out, so be it. All mistakes in these notes are mine. If something is quite useful, it is stolen from somewhere else.

You can simply take these notes and read them. After doing so, you will at least have seen the basic concepts, and be able to recognize them in the literature. But a much better approach is to read these notes and use them as a start for further study. This could mean going to the library and looking up these topics in a number of books on thermodynamics. Nothing helps understanding more than seeing different descriptions of the same material. If there is one skill that is currently missing among many students, it is the capability of really using a library! Also, I do not want to give you examples of what I consider good textbooks. You should go find out. My opinion would be a single biased opinion anyhow.

These notes started when I summarized discussions in class. In the current form, I present them as reading material, to start class discussions. Thermodynamics can be taught easily in a non-lecture approach, and I am working on including more questions which could be discussed in class (they are especially lacking in the later parts). Although students feel uneasy with this approach, having a fear that they miss something important, they should realize that the purpose of these notes is to make sure that all important material is in front of them. Class discussions, of course, have to be guided. Sometimes a discussion goes in the wrong direction. This is fine for a while, but than the instructor should help bring it back to the correct path. Of course, the analysis of why the discussion took a wrong turn is extremely valuable, because one learns most often from one's mistakes (at least, one should).

The material in these notes is sufficient for a quarter or a semester course. In a semester course one simply adds expansions to selected topics. Also, the material should be accessible for seniors and first year graduate students. The mathematics involved is not hard, but calculus with many partial derivatives is always a bit confusing for everybody, and functional derivatives also need a bit of review. It is assumed that basic material covered in the introductory physics

sequence is known, hence students should have some idea about temperature and entropy. Apart from that, visit the library and discover some lower level texts on thermodynamics. Again, there are many good ones. And, if these textbooks are more than ten years old, do not discard them, because they are still as relevant as they were before. On the other hand, if you use the web as a source of information, be aware that there are many web-sites posted by well-meaning individuals, which are full of wrong information. Nevertheless, browsing the web is a good exercise, since nothing is more important than to learn to recognize which information is incorrect!

Problem solving is very important in physics, and in order to obtain a working knowledge of thermodynamics it is important to be able to do problems. Many problems are included, most of them with solutions. It is good to start problems in class, and to have a discussion of the general approach that needs to be taken. When solving problems, for most people it is very beneficial to work in groups, and that is encouraged. When you try to solve a problem and you get stuck, do not look at the solution! Go to other textbooks and try to find material that pertains to your problem. When you believe that you have found the solution, then it is time to compare with the solution in the notes, and then you can check if the solution in the notes is correct.

In many cases, solving problems in thermodynamics always follows the same general path. First you identify the independent state variables. If an experiment is performed at constant temperature, temperature is an independent state variable because it is controlled. Control means that either we can set it at a certain value, or that we can prevent changes in the variable. For example, if we discuss a gas in a closed container, the volume of the gas is an independent state variable, since the presence of the container makes it impossible for the gas to expand or contract. Pressure, on the other hand, is not an independent state variable in this example, since we have no means of controlling it. Second, based on our determination of independent state variables, we select the correct thermodynamic potential to work with. Finally, we calculate the response functions using this potential, and find relations between these functions. Or we use these response functions to construct equations of state using measured data. And so on.

Work in progress is adding more questions in the main text. There are more in the beginning than in the end, a common phenomenon. As part of their assignments, I asked students which questions they would introduce. These questions are collected in an appendix. So, one should not take these questions as questions from the students (although quite a few are), but also as questions that the students think are good to ask! In addition, I asked students to give a summary of each chapter. These responses are also given in an appendix.

I provided this material in the appendices, because I think it is useful in two different ways. If you are a student studying thermodynamics, it is good to know what others at your level in the educational system think. If you are struggling with a concept, it is reassuring to see that others are too, and to see with what kind of questions they came up to find a way out. In a similar manner, it it helpful to see what others picked out as the most important part

of each chapter. By providing the summaries I do not say that I agree with them (in fact, sometimes I do not)(Dutchmen rarely agree anyhow), but it gives a standard for what others picked out as important. And on the other hand, if you are teaching this course, seeing what students perceive is extremely helpful.

Finally, a thanks to all students who took my classes. Your input has been essential, your questions have lead to a better understanding of the material, and your research interests made me include a number of topics in these notes which otherwise would have been left out.

History of these notes:

1991 Original notes for first three chapters written using the program EXP.

1992 Extra notes developed for chapters four and five.

2001 Notes on chapters four and five expanded.

2002 Notes converted to LaTeX, significantly updated, and chapter six added.

2003 Notes corrected, minor additions to first five chapters, some additions to chapter six.

Chapter 1

Basic Thermodynamics.

1.1 Introduction.

What state am I in?

SIMPLE BEGINNINGS.

In the mechanical world of the 19th century, physics was very easy. All you needed to know were the forces acting on particles. After that it was simply $F = ma$. Although this formalism is not hard, actual calculations are only feasible when the system under consideration contains a few particles. For example, the motion of solid objects can be described this way if they are considered to be point particles. In this context, we have all played with Lagrangians and Hamiltonians. Liquids and gases, however, are harder to deal with, and are often described in a continuum approximation. Everywhere in space one defines a mass density and a velocity field. The continuity and Newton's equations then lead to the time evolution of the flow in the liquid.

ASKING THE RIGHT QUESTIONS.

The big difference between a solid and a liquid is complexity. In first approximation a solid can be described by six coordinates (center of mass, orientation), while a liquid needs a mass density field which is essentially an infinite set of coordinates. The calculation of the motion of a solid is relatively easy, especially if one uses conservation laws for energy, momentum, and angular momentum. The calculation of the flow of liquids is still hard, even today, and is often done on computers using finite difference or finite element methods. In the 19th century, only the simplest flow patterns could be analyzed. In many cases these

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flow patterns are only details of the overall behavior of a liquid. Very often one is interested in more general quantities describing liquids and gases. In the 19th century many important questions have been raised in connection with liquids and gases, in the context of steam engines. How efficient can a steam engine be? Which temperature should it operate at? Hence the problem is what we need to know about liquids and gases to be able to answer these fundamental questions.

Divide and conquer.

In thermodynamics we consider <u>macroscopic</u> systems, or systems with a large number of degrees of freedom. Liquids and gases certainly belong to this class of systems, even if one does not believe in an atomic model! The only requirement is that the system needs a description in terms of density and velocity fields.

Solids can be described this way. In this case the mass density field is given by a constant plus a small variation. The time evolution of these deviations from equilibrium shows oscillatory patterns, as expected. The big difference between a solid and a fluid is that the deviations from average in a solid are small and can be ignored in first approximation.

No details, please.

In a thermodynamic theory we are never interested in the detailed functional form of the density as a function of position, but only in macroscopic or global averages. Typical quantities of interest are the volume, magnetic moment, and electric dipole moment of a system. These macroscopic quantities, which can be measured, are called <u>thermodynamic</u> or <u>state</u> variables. They uniquely determine the <u>thermodynamic state</u> of a system.

State of a system.

The definition of the state of a system is in terms of operations. What are the possible quantities which we can measure? In other words, how do we assign numbers to the fields describing a material? Are there any problems? For example, one might think that it is easy to measure the volume of a liquid in a beaker. But how does this work close to the critical point where the index of refraction of the liquid and vapor become the same? How does this work if there is no gravity? In thermodynamics we simply assume that we are able to measure some basic quantities like volume.

Another question is how many state variables do we need to describe a system. For example we prepare a certain amount of water and pour it in a beaker, which we cap. The next morning we find that the water is frozen. It is obvious that the water is not in the same state, and that the information we had about the system was insufficient to uniquely define the state of the system.

In this case we omitted temperature.

It can be more complicated, though. Suppose we have prepared many iron bars always at the same shape, volume, mass, and temperature. They all look the same. But then we notice that some bars affect a compass needle while others do not. Hence not all bars are the same and we need additional information to uniquely define the state of the bar. Using the compass needle we can measure the magnetic field and hence we find the magnetic moment of the bar.

In a next step we use all bars with a given magnetic moment. We apply a force on these bars and see how much they expand, from which we calculate the elastic constants of the bar. We find that different bars have different values of the elastic constants. What are we missing in terms of state variables? This is certainly not obvious. We need information about defects in the structure, or information about the mass density field beyond the average value.

Was I in a different state before?

IS IT CHANGING?

At this point it is important to realize that a measured value of a state variable is always a time-average. The pressure in an ideal gas fluctuates, but the time scale of the fluctuations is much smaller than the time scale of the externally applied pressure changes. Hence these short time fluctuations can be ignored and are averaged out in a measurement. This does imply a warning, though. If the fluctuations in the state variables are on a time scale comparable with the duration of the experiment a standard thermodynamic description is useless.

HOW DO WE CHANGE?

The values of the state variables for a given system can be modified by applying forces. An increase in pressure will decrease the volume, a change in magnetic induction will alter the magnetic moment. The pressure in a gas in a container is in many cases equal to the pressure that this container exerts on the gas in order to keep it within the volume of the container. It is possible to use this pressure to describe the state of the system and hence pressure (and magnetic induction) are also state variables. One basic question in thermodynamics is how these state variables change when external forces are applied. In a more general way, if a specific state variable is changed by external means, how do the other state variables respond?

NUMBER OF VARIABLES, AGAIN.

The number of state variables we need to describe the state of a system depends on the nature of that system. We expand somewhat more on the previous discussion. An ideal gas, for example, is in general completely characterized by its volume, pressure, and temperature. It is always possible to add more state variables to this list. Perhaps one decides to measure the magnetic moment of an ideal gas too. Obviously, that changes our knowledge of the state of the ideal gas. If the value of this additional state variable is always the same, no matter what we do in our experiment, then this variable is not essential. But one can always design experiments in which this state variable becomes essential. The magnetic moment is usually measured by applying a very small magnetic induction to the system. This external field should be zero for all purposes. If it is not, then we have to add the magnetic moment to our list of state variables.

It is also possible that one is not aware of additional essential state variables. Experiments will often indicate that more variables are needed. An example is an experiment in which we measure the properties of a piece of iron as a function of volume, pressure, and temperature. At a temperature of about $770°C$ some abnormal behavior is observed. As it turns out, iron is magnetic below this temperature and in order to describe the state of an iron sample one has to include the magnetic moment in the list of essential state variables. An ideal gas in a closed container is a simple system, but if the gas is allowed to escape via a valve, the number of particles in this gas also becomes an essential state variable needed to describe the state of the system inside the container.

Are measured values always spatial averages?

Are there further classifications of states or processes?

1.2   Some definitions.

Two types of processes.

If one takes a block of wood, and splits it into two pieces, one has performed a simple action. On the level of thermodynamic variables one writes something like $V = V_1 + V_2$ for the volumes and similar equations for other state variables. The detailed nature of this process is, however, not accessible in this language. In addition, if we put the two pieces back together again, they do in general not stay together. The process was irreversible. In general, in thermodynamics one only studies the reversible behavior of macroscopic systems. An example would

be the study of the liquid to vapor transition. Material is slowly transported from one phase to another and can go back if the causes are reversed. The state variables one needs to consider in this case are the pressure, temperature, volume, interface area (because of surface tension), and perhaps others in more complicated situations.

WHEN THERE IS NO CHANGE.

Obviously, all macroscopic systems change as a function of time. Most of these changes, however, are on a microscopic level and are not of interest. We are not able to measure them directly. Therefore, in thermodynamics one defines a steady state when all thermodynamic variables are independent of time. A resistor connected to a constant voltage is in a steady state. The current through the resistor is constant and although there is a flow of charge, there are no net changes in the resistor. The same amount of charge comes in as goes out. Thermodynamic equilibrium describes a more restricted situation. A system is in thermodynamic equilibrium if it is in a steady state and if there are no *net macroscopic* currents (of energy, particles, etc) over macroscopic distances. There is some ambiguity in this definition, connected to the scale and magnitude of the currents. A vapor-liquid interface like the ocean, with large waves, is clearly not in equilibrium. But how small do the waves have to be in order that we can say that the system is in equilibrium? Also, the macroscopic currents might be very small. Glass, for example, is not in thermal equilibrium according to a strict definition, but the changes are very slow with a time scale of hundreds of years. Hence even if we cannot measure macroscopic currents, they might be there. We will in general ignore these situations, since they tend not to be of interest *on the time scale of the experiments!*

What do you think about hysteresis loops in magnets?

STATE FUNCTIONS.

Once we understand the nature of thermal equilibrium, we can generalize the concept of state variables. A state function is any quantity which *in thermodynamic equilibrium* only depends on the values of the state variables and not on the history (or future?) of the sample. A simple state function would be the product of the pressure and volume. This product has a physical interpretation, but cannot be measured *directly*.

TWO TYPES OF VARIABLES.

Thermodynamic variables come in two varieties. If one takes a system in

equilibrium the volume of the left half is only half the total volume (surprise) but the pressure in the left half is equal to the pressure of the total system. There are only two possibilities. Either a state variable scales linearly with the size of the system, or is independent of the size of the system. In other words, if we consider two systems in *thermal equilibrium*, made of identical material, one with volume V_1 and one with volume V_2, a state variable X either obeys $\frac{X_1}{V_1} = \frac{X_2}{V_2}$ or $X_1 = X_2$. In the first case the state variable is called <u>extensive</u> and in the second case it is called <u>intensive</u>. Extensive state variables correspond to generalized displacements. For the volume this is easy to understand; increasing volume means displacing outside material and doing work on it in the process. Intensive state variables correspond to generalized forces. The pressure is the force needed to change the volume. For each extensive state variable there is a corresponding intensive state variable and vice-versa.

THERMODYNAMIC LIMIT.

At this point we are able to define what we mean by a large system. Ratios of an extensive state variable and the volume, like $\frac{X}{V}$, are often called <u>densities</u>. It is customary to write these densities in lower case, $x = \frac{X}{V}$. If the volume is too small, x will depend on the volume. Since X is extensive, this is not supposed to be the case. In order to get rid of the effects of a finite volume (surface effects!) one has to take the limit $V \rightarrow \infty$. This is called the <u>thermodynamic limit</u>. All our mathematical formulas are strictly speaking only correct in this limit. In practice, this means that the volume has to be large enough in order that changes in the volume do not change the densities anymore. It is always possible to write $x(V) = x_\infty + \alpha V^{-1} + \mathcal{O}(V^{-2})$. The magnitude of α decides which value of the volume is large enough.

PHYSICS DETERMINES THE RELATION BETWEEN STATE VARIABLES.

Why are all these definitions important? So far we have not discussed any physics. If all the state variables would be independent we could stop right here. Fortunately, they are not. Some state variables are related by <u>equations of state</u> and these equations contain the physics of the system. It is important to note that these equations of state only relate the values of the state variables *when the system is in thermal equilibrium, in the thermodynamic limit*! If a system is not in equilibrium, any combination of state variables is possible. It is even possible to construct non-equilibrium systems in which the actual definition or measurement of certain state variables is not useful or becomes ambiguous.

Simple examples of equations of state are the ideal gas law $pV = NRT$ and Curie's law $M = \frac{CNH}{T}$. The first equation relates the product of the pressure p and volume V of an ideal gas to the number of moles of gas N and the temperature T. The constant of proportionality, R, is the molar gas constant, which is the product of Boltzmann's constant k_B and Avogadro's number N_A. The second equation relates the magnetic moment M to the number of moles

of atoms N, the magnetic field H, and the temperature T. The constant of proportionality is Curie's constant C. Note that in thermodynamics the preferred way of measuring the amount of material is in terms of moles, which again can be defined independent of a molecular model.

How do we get equations of state?

Equations of state have two origins. One can completely ignore the microscopic nature of matter and simply postulate some relation. One then uses the laws of thermodynamics to derive functional forms for specific state variables as a function of the others, and compares the predicted results with experiment. The ideal gas law has this origin. This procedure is exactly what is done in thermodynamics. One does not need a model for the detailed nature of the systems, but derives general conclusions based on the average macroscopic behavior of a system in the thermodynamic limit.

In order to derive equations of state, however, one has to consider the microscopic aspects of a system. Our present belief is that all systems consist of atoms. If we know the forces between the atoms, the theory of statistical mechanics will tell us how to derive equations of state. There is again a choice here. It is possible to postulate the forces. The equations of state could then be derived from molecular dynamics calculations, for example. The other route derives these effective forces from the laws of quantum mechanics and the structure of the atoms in terms of electrons and nuclei. The interactions between the particles in the atoms are simple Coulomb interactions in most cases. These Coulomb interactions follow from yet a deeper theory, quantum electro-dynamics, and are only a first approximation. These corrections are almost always unimportant in the study of materials and only show up at higher energies in nuclear physics experiments.

Why do we need equations of state?

Equations of states can be used to classify materials. They can be used to derive atomic properties of materials. For example, at low densities a gas of helium atoms and a gas of methane atoms both follow the ideal gas law. This indicates that in this limit the internal structure of the molecules does not affect the motion of the molecules! In both cases they seem to behave like point particles. Later we will see that other quantities are different. For example, the internal energy certainly is larger for methane where rotations and translations play a role.

Classification of changes of state.

Since a static universe is not very interesting, one has to consider changes in the state variables. In a <u>thermodynamic transformation or process</u> a system

changes one or more of its state variables. A spontaneous process takes place
without any change in the external constraints. In an adiabatic process no
heat is exchanged between the system and the environment. A process is called
isothermal if the temperature of the system remains the same, isobaric if the
pressure does not change, and isochoric if the mass density (the number of moles
of particles divided by the volume) is constant. If the change in the system is
infinitesimally slow, the process is quasistatic .

Reversible process.

The most important class of processes are those in which the system starts
in equilibrium, the process is quasistatic, and all the intermediate states and the
final state are in equilibrium. These processes are called reversible. The process
can be described by a continuous path in the space of the state variables, and
this path is restricted to the surfaces determined by the equations of state for
the system. By inverting all external forces, the path in the space of the state
functions will be reversed, which prompted the name for this type of process.
Reversible processes are important because they can be described mathemati-
cally via the equations of state. This property is lost for an irreversible process
between two equilibrium states, where we only have a useful mathematical de-
scription of the initial and final state. As we will see later, the second law of
thermodynamics makes another distinction between reversible and irreversible
processes.

How does a process become irreversible?

An irreversible process is either a process which happens too fast or which is
discontinuous. The sudden opening of a valve is an example of the last case. The
system starts out in equilibrium with volume V_i and ends in equilibrium with
a larger volume V_f. For the intermediate states the volume is not well defined,
though. Such a process takes us outside of the space of state variables we
consider. It can still be described in the phase space of all system variables, and
mathematically it is possible to define the volume, but details of this definition
will play a role in the description of the process. Another type of irreversible
process is the same expansion from V_i to V_f in a controlled way. The volume
is well-defined everywhere in the process, but the system is not in equilibrium
in the intermediate states. The process is going too fast. In an ideal gas this
would mean, for example, $pV \neq NRT$ for the intermediate stages.

Are there general principles connecting the values of state variables, valid for
all systems?

1.3 Zeroth Law of Thermodynamics.

GENERAL RELATIONS.

An equation of state specifies a relation between state variables which holds for a certain system. It represents the physics particular to that system. There are, however, a few relations that hold for all systems, independent of the nature of the system. Following an old tradition, these relations are called the laws of thermodynamics. There are four of them, numbered 0 through 3. The middle two are the most important, and they have been paraphrased in the following way. Law one tells you that in the game of thermodynamics you cannot win. The second law makes it even worse, you cannot break even.

LAW ZERO.

The zeroth law is relatively trivial. It discusses systems in equilibrium. Two systems are in thermal equilibrium if they are in contact and the total system, encompassing the two systems as subsystems, is in equilibrium. In other words, two systems in contact are in equilibrium if the individual systems are in equilibrium and there are no net macroscopic currents between the systems. The zeroth law states that if equilibrium system A is in contact and in equilibrium with systems B and C (not necessarily at the same time, but A does not change), then systems B and C are also in equilibrium with each other. If B and C are not in contact, it would mean that if we bring them in contact no net macroscopic currents will flow.

SIGNIFICANCE OF LAW ZERO.

The importance of this law is that it enables to define universal standards for temperature, pressure, etc. If two different systems cause the same reading on the same thermometer, they have the same temperature. A temperature scale on a new thermometer can be set by comparing it with systems of known temperature.

Are there any consequences for the sizes of the systems?

1.4 First law: Energy.

HEAT IS ENERGY FLOW.

The first law of thermodynamics states that energy is conserved. The change in internal energy U of a system is equal to the amount of heat energy added to the system minus the amount of work done by the system. It implies that heat is a form of energy. Technically, heat describes the flow of energy, but we are very sloppy in our use of words here. The formal statement of the first law is

$$dU = \bar{d}Q - \bar{d}W \tag{1.1}$$

The amount of heat added to the system is $\bar{d}Q$ and the amount of work done by the system is $\bar{d}W$. The mathematical formulation of the first law also shows an important characteristic of thermodynamics. It is often only possible to define thermodynamic relations via changes in the thermodynamic quantities.

The internal energy is a state variable.

The internal energy U is a state variable and an infinitesimal change in internal energy is an exact differential. Since U is a state variable, the value of any integral $\int dU$ depends only on the values of U at the endpoints of the path in the space of state variables, and not on the specific path between the endpoints. The internal energy U has to be a state variable, or else we could devise a process in which a system goes through a cycle and returns to its original state while loosing or gaining energy. For example, this could mean that a burning piece of coal today would produce less heat than tomorrow. If the internal energy would not be a state variable, we would have sources of free energy.

Exact differentials.

The concept of exact differentials is important, and hence we will illustrate it by some examples. Assume the function f is a state function of the state variables x and y only, f(x,y). For small changes we can write

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{1.2}$$

where in the notation for the partial derivatives the variable which is kept constant is also indicated. This is always very useful in thermodynamics, because one often changes variables. There would be no problems if quantities were defined directly like $f(x, y) = x + y$. In thermodynamics, however, most quantities are defined by small changes in a system. Hence, suppose the change in a quantity g is related to changes in the state variables x and y via

$$\bar{d}g = h(x, y)dx + k(x, y)dy \tag{1.3}$$

Is the quantity g a state function, in other words is g uniquely determined by the state of a system or does it depend on the history, on how the system got into that state? A necessary and sufficient condition for g to be a state function is that

$$\left(\frac{\partial h}{\partial y}\right)_x = \left(\frac{\partial k}{\partial x}\right)_y \tag{1.4}$$

The necessity follows immediately from 1.2, assuming that the partial derivatives in 1.4 exist and are continuous. This is because in second order derivatives we can interchange the order of the derivatives under such conditions. That it is sufficient can be shown as follows. Consider a path $(x,y) = (\phi(t), \psi(t))$ from (x_1, y_1) at t_1 to (x_2, y_2) at t_2 and integrate $\bar{d}g$, using $dx = \frac{d\phi}{dt}dt$, $dy = \frac{d\psi}{dt}dt$,

$$\int_{t_1}^{t_2} \left(h(\phi(t), \psi(t)) \frac{d\phi}{dt} + k(\phi(t), \psi(t)) \frac{d\psi}{dt} \right) dt \tag{1.5}$$

Define

$$H(x,y) = \int_0^x dx' h(x', y) + \int_0^y dy' k(0, y') \tag{1.6}$$

and $\mathcal{H}(t) = H(\phi(t), \psi(t))$. It follows that

$$\frac{d\mathcal{H}}{dt} = \left(\frac{\partial H}{\partial x}\right)_y \frac{d\phi}{dt} + \left(\frac{\partial H}{\partial y}\right)_x \frac{d\psi}{dt} \tag{1.7}$$

The partial derivatives of H are easy to calculate:

$$\left(\frac{\partial H}{\partial x}\right)_y (x,y) = h(x,y) \tag{1.8}$$

$$\left(\frac{\partial H}{\partial y}\right)_x (x,y) = \int_0^x dx' \left(\frac{\partial h}{\partial y}\right)_x (x', y) + k(0,y) =$$
$$\int_0^x dx' \left(\frac{\partial k}{\partial x}\right)_y (x', y) + k(0,y) = k(x,y) \tag{1.9}$$

Hence the integral of $\bar{d}g$ is equal to $\mathcal{H}(t_2) - \mathcal{H}(t_1)$ which does not depend on the path taken between the end-points of the integration.

EXAMPLE.

An example might illustrate this better. Suppose x and y are two state variables, and they determine the internal energy completely. If we define changes in the internal energy via changes in the state variables x and y via

$$dU = x^2 y dx + \frac{1}{3}x^3 dy \tag{1.10}$$

we see immediately that this definition is correct, the energy U is a state function. The partial derivatives obey the symmetry relation 1.4 and one can simply integrate dU to get $U(x,y) = \frac{1}{3}x^3 y + U_0$.

The changes in heat and work could be related in the following way

$$\bar{d}Q = \frac{1}{2}x^2 y \, dx + \frac{1}{2}x^3 \, dy \tag{1.11}$$

$$\bar{d}W = -\frac{1}{2}x^2 y \, dx + \frac{1}{6}x^3 \, dy \tag{1.12}$$

These definitions do indeed obey the first law 1.1. It is also clear using the symmetry relation 1.4 that these differentials are not exact.

Suppose the system which is described above is originally in the state $(x, y) = (0, 0)$. Now we change the state of the system by a continuous transformation from $(0, 0)$ to $(1, 1)$. We do this in two different ways, however. Path one takes us from $(0, 0)$ to $(0, 1)$ to $(1, 1)$ along two straight line segments, path two is similar from $(0, 0)$ to $(1, 0)$ to $(1, 1)$. The integrals for dU, $\bar{d}Q$, and $\bar{d}W$ are easy, since along each part of each path either dx or dy is zero.

First take path one.

$$U(1, 1) - U(0, 0) = \int_0^1 dy \frac{1}{3}(0)^3 + \int_0^1 dx \, x^2 1 = \frac{1}{3} \tag{1.13}$$

$$\Delta Q = \int_0^1 dy \frac{1}{2}(0)^3 + \int_0^1 dx \frac{1}{2}x^2 1 = \frac{1}{6} \tag{1.14}$$

$$\Delta W = \int_0^1 dy \frac{1}{6}(0)^3 + \int_0^1 dx (-\frac{1}{2})x^2 1 = -\frac{1}{6} \tag{1.15}$$

First of all, the change in U is consistent with the state function we found, $U(x, y) = \frac{1}{3}x^3 y + U_0$. Second, we have $\Delta U = \Delta Q - \Delta W$ indeed. It is easy to calculate that for the second path we have $\Delta U = \frac{1}{3}$, $\Delta Q = \frac{1}{2}$, and $\Delta W = \frac{1}{6}$. The change in internal energy is indeed the same, and the first law is again satisfied.

IMPORTANCE OF Q AND W NOT BEING STATE FUNCTIONS.

Life on earth would have been very different if Q and W would have been state variables. Steam engines would not exist, and you can imagine all consequences of that fact.

Expand on the consequences of Q and W being state functions

Any engine repeats a certain cycle over and over again. A complete cycle in our example above might be represented by a series of continuous changes in the state variables (x,y) like $(0, 0) \to (0, 1) \to (1, 1) \to (1, 0) \to (0, 0)$. After the completion of one cycle, the energy U is the same as at the start of the cycle. The change in heat for this cycle is $\Delta Q = \frac{1}{6} - \frac{1}{2} = -\frac{1}{3}$ and the work done on

the environment is $\Delta W = -\frac{1}{6} - \frac{1}{6} = -\frac{1}{3}$. This cycle represents a heater: since ΔQ is negative, heat is added to the environment and since ΔW is negative the environment does work on the system. Running the cycle in the opposite direction yields an engine converting heat into work. If Q and W would be state variables, for each complete cycle we would have $\Delta Q = \Delta W = 0$, and no net change of work into heat and vice-versa would be possible!

When was the first steam engine constructed?

Work can be done in many different ways. A change in any of the extensive state variables of the system will cause a change in energy, or needs a force in order that it happens. Consider a system with volume V, surface area A, polarization $\vec{P}$, magnetic moment $\vec{M}$, and number of moles of material N. The work done *by the system on the environment* is

$$\bar{d}W = pdV - \sigma dA - \vec{E}d\vec{P} - \vec{H}d\vec{M} - \mu dN \qquad (1.16)$$

where the forces are related to the intensive variables pressure p, surface tension σ, electric field $\vec{E}$, magnetic field $\vec{H}$, and chemical potential μ. Note that some textbooks treat the μdN term in a special way. There is, however, no formal need to do so. The general form is

$$\bar{d}W = -\sum_j x_j dX_j \qquad (1.17)$$

where the generalized force x_j causes a generalized displacement dX_j in the state variable X_j. Note that the pdV term has the opposite sign from all others. A positive pressure decreases the volume, while a positive magnetic field increases the magnetic magnetization in general. This difference in sign is historical, and is justified by the old, intuitive definitions of pressure and other quantities.

1.5 Second law: Entropy.

CLAUSIUS AND KELVIN.

The second law of thermodynamics tells us that life is not free. According to the first law we can change heat into work, apparently without limits. The second law, however, puts restrictions on this exchange. There are two versions of the second law, due to Kelvin and Clausius. Clausius stated that *there are no thermodynamic processes in which the only net change is a transfer of heat from one reservoir to a second reservoir which has a higher temperature.* Kelvin formulated it in a different way: *there are no thermodynamic processes in which the only effect is to extract a certain amount of heat from a reservoir and convert*

it completely into work. The opposite is possible, though. These two statements are equivalent as we will see.

HEAT IS A SPECIAL FORM OF ENERGY EXCHANGE.

The second law singles out heat as compared to all other forms of energy. Since work is defined via a change in the extensive state variables, we can think of heat as a change of the internal degrees of freedom of the system. Hence heat represents all the degrees of freedom we have swept under the rug when we limited state variables to measurable, average macroscopic quantities. The only reason that we can say anything at all about heat is that it is connected to an extremely large number of variables (because of the thermodynamic limit). In that case the mathematical laws of large numbers apply, and the statements about heat become purely statistical. In statistical mechanics we will return to this point. Note that the second law does not limit the exchange of energy switching from one form of work to another. In principal we could change mechanical work into electrical work without penalty! In practice, heat is always generated.

HEAT AS A MEASURABLE QUANTITY.

One important implicit assumption in these statements is that a large outside world does exist. In the first law we define the change of energy via an exchange of heat and work with the outside world. Hence we assume that there is something outside our system. As a consequence, the second law does not apply to the universe as a whole.

The definitions of heat and entropy in thermodynamics are based on quantities that we can measure. They are operational definitions. The second law is an experimental observation, which has never been falsified in macroscopic experiments. Maxwell started an important discussion trying to falsify the second law on a microscopic basis (his famous demon), but that never worked either. It did lead to important statements about computing, though!

If the second law is universally valid, it defines a preferred direction of time (by increasing entropy or energy stored in the unusable internal variables), and seems to imply that every system will die a heat death. This is not true, however, because we always invoke an outside world, and at some point heat will have to flow from the system to the outside. This is another interesting point of discussion in the philosophy of science.

In statistical mechanics we can define entropy and energy by considering the system only, and is seems possible to define the entropy of the universe in that way. Here one has to keep in mind that the connection between statistical mechanics and thermodynamics has to be made, and as soon as we make that connection we invoke an outside world. This is an interesting point of debate, too, which takes place on the same level as the debate in quantum mechanics about the interpretation of wave functions and changes in the wave functions.
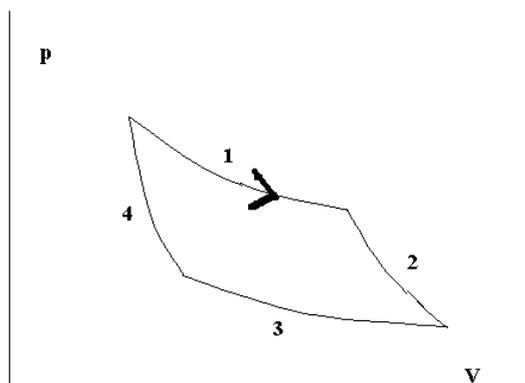
Figure 1.1: **Carnot cycle in PV diagram .**

CARNOT ENGINE.

An engine is a system which changes its thermodynamic state in cycles and converts heat into work by doing so. A *Carnot engine* is any system repeating the following <u>reversible</u> cycle: (1) an isothermal expansion at a high temperature T_1, (2) an adiabatic expansion in which the temperature is lowered to T_2, (3) an isothermal contraction at temperature T_2, and finally (4) an adiabatic contraction back to the initial state. In this case work is done using a change in volume. Similar Carnot engines can be defined for all other types of work. It is easiest to talk about Carnot engines using the pressure p, the volume V, and the temperature T as variables. A diagram of a Carnot engine in the pV plane is shown in figure 1.1.

The material in a Carnot engine can be anything. For practical reasons it is often a gas. Also, because steps one and three are isothermal, contact with a heat reservoir is required, and the Carnot engine operates between these two heat reservoirs, by definition. Mechanical work is done in all four parts of the cycle. We can define Carnot engines for any type of work, but mechanical work is the easiest to visualize (and construction of Carnot engines based on mechanical work is also most common).

CARNOT ENGINES ARE THE MOST EFFICIENT!

The second law of thermodynamics has a very important consequence for Carnot engines. One can show that *a Carnot engine is the most efficient engine operating between two reservoirs at temperature T_1 and T_2*! This is a very strong statement, based on minimal information. The efficiency η is the ratio of the work W performed on the outside world and the heat Q_1 absorbed by the system in the isothermal step one at high temperature. Remember that in steps two
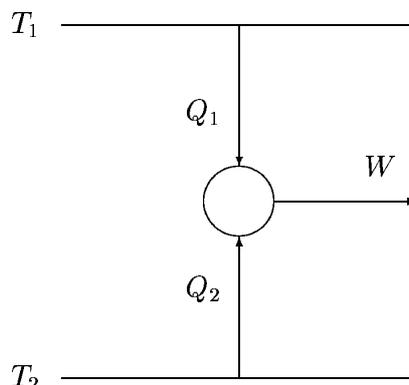
Figure 1.2: **Schematics of a Carnot engine.**

and four no heat is exchanged. The heat absorbed from the reservoir at low temperature in step three is Q_2 and the first law tells us that $W = Q_1 + Q_2$. We define the flow of heat Q_i to be <u>positive</u> when heat flows <u>into</u> the system. In most engines we will, of course, have $Q_1 > 0$ and $Q_2 < 0$. This gives us

$$\eta = \frac{W}{Q_1} = 1 + \frac{Q_2}{Q_1} \tag{1.18}$$

Work is positive when it represents a flow of energy to the outside world. A Carnot engine in reverse is a heater (or refrigerator depending on which reservoir you look at).

Can the efficiency be greater than one?

A Carnot engine can be represented in as follows, see figure 1.2. In this figure the arrows point in the direction in which the energy flow is defined to be positive.

EQUIVALENCY OF CLAUSIUS AND KELVIN.

The two formulations of the second law of Clausius and Kelvin are equivalent. If a Kelvin engine existed which converts heat completely into work, this work can be transformed into heat dumped into a reservoir at higher temperature, in contradiction with Clausius. If a Clausius process would exist, we can use it to store energy at a higher temperature. A normal engine would take this amount of heat, dump heat at the low temperature again while performing work, and there would be a contradiction with Kelvin's formulation of the second law. The statement about Carnot engines is shown to be true in a similar way.
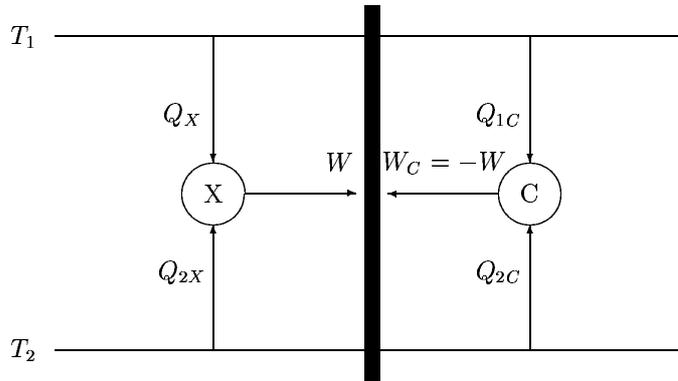
Figure 1.3: **Two engines feeding eachother.**

Contradictions if existence of more efficient engine.

Assume that we have an engine X which is more efficient than a Carnot engine C. We will use this engine X to drive a Carnot engine in reverse, see figure 1.3. The engine X takes an amount of heat $Q_X > 0$ from a reservoir at high temperature. It produces an amount of work $W = \eta_X Q_X > 0$ and takes an amount of heat $Q_{2X} = (\eta_X - 1)Q_X$ from the reservoir at low temperature. Notice that we need $\eta_X < 1$, (and hence $Q_{2X} < 0$), otherwise we would violate Kelvin's formulation of the second law. This means that the net flow of heat is towards the reservoir of low temperature. Now take a Carnot engine operating between the same two reservoirs. This Carnot engine is driven by the amount of work W, hence the amount of work performed by the Carnot engine is $W_C = -W$. This Carnot engine takes an amount of heat $Q_{1C} = \frac{W_C}{\eta_C} = -\frac{\eta_X}{\eta_C}Q_X$ from the reservoir at high temperature and an amount $Q_{2C} = W_C - Q_{1C} = (\frac{1}{\eta_C} - 1)\eta_X Q_X$ from the reservoir at low temperature. Now consider the combination of these two engines. This is a machine which takes an amount of heat $(1-\frac{\eta_x}{\eta_c})Q_x$ from the reservoir at high temperature and the opposite amount from the reservoir at low temperature. Energy is conserved, but Clausius tells us that the amount heat taken from the high temperature reservoir should be positive, or $\eta_x \leq \eta_c$. Hence a Carnot engine is the most efficient engine which one can construct!

In a different proof we can combine an engine X and a Carnot engine, but require $Q_{2X} + Q_{2C} = 0$. Such an engine produces an amount of work W_{net} which has to be negative according to Kelvin.

Show that this implies $\eta_X \leq \eta_C$.

ALL CARNOT ENGINES ARE EQUALLY EFFICIENT.

One can easily show that all Carnot engines have the same efficiency. Suppose the efficiencies of Carnot engine one and two are η_1 and η_2, respectively. Use one Carnot engine to drive the other in reverse, and it follows that we need $\eta_1 \leq \eta_2$ and also $\eta_2 \leq \eta_1$, or $\eta_1 = \eta_2$. Hence the efficiency of an arbitrary Carnot engine is η_C. This is independent of the details of the Carnot engine, except that it should operate between a reservoir at T_1 and a reservoir at T_2. These are the only two variables which play a role, and the Carnot efficiency should depend on them only: $\eta_C(T_1, T_2)$.

CARNOT EFFICIENCY CAN BE MEASURED EXPERIMENTALLY.

This efficiency function can be determined experimentally by measuring Q and W flowing in and out a given Carnot engine. How? That is a problem. First, consider the work done. This is the easier part. For example, because of the work done a weight is lifted a certain distance. This gives us the change in energy, and hence the work done. In order to use this type of measurement, however, we need to know details about the type of work. This is essentially the same as saying that we need to understand the measurements we are doing.

How do we measure heat? We need a reference. For example, take a large closed glass container with water and ice, initially in a one to one ratio. Assume that the amount of energy to melt a unit mass of ice is our basic energy value. We can measure the amount of heat that went into this reference system by measuring the change in the volumes of water and ice. Also, if a sample of unknown temperature is brought into contact with the reference system, we can easily determine whether the temperature of the sample is higher of lower that the reference temperature of the water and ice system. If it is higher, ice will melt, if it is lower, water will freeze. Note that we assume that the temperature of the reference system is positive!

EXPERIMENTAL DEFINITION OF TEMPERATURE.

State variables are average, macroscopic quantities of a system which can be measured. This is certainly a good definition of variables like volume, pressure, and number of particles. They are related to basic concepts like length, mass, charge, and time. Temperature is a different quantity, however. A practical definition of the temperature of an object is via a thermometer. The active substance in the thermometer could be mercury or some ideal gas. But those are definitions which already incorporate some physics, like the linear expansion of solids for mercury or the ideal gas law for a gas. It is different from the definitions of length and time in terms of the standard meter and clock. In a similar vein we would like to define temperature as the result of a measurement of a comparison with a standard. Hence we assume that we have a known object

of temperature T_0, similar to the standard meter and clock. An example would be the container with the water and ice mixture mentioned above.

Now how do we compare temperatures on a quantitative level? If we want to find the temperature of an object of unknown temperature T, we take a Carnot engine and operate that engine between the object and the standard. We measure the amount of heat Q flowing from the reference system to the Carnot engine and the amount of work W done by the Carnot engine. The ratio of these two quantities is the efficiency of the Carnot engine, which only depends on the two temperatures.

If the temperature of the reference system is higher that the temperature of the object, we use the reference system as the high temperature reservoir and find:

$$\eta_C = \frac{W}{Q} \qquad (1.19)$$

If the temperature of the reference system is lower that the temperature of the object, we use the reference system as the low temperature reservoir and find:

$$\eta_C = \frac{W}{W - Q} \qquad (1.20)$$

In the first case we assign a temperature T to the object according to

$$\frac{T}{T_0} = (1 - \eta_C) \qquad (1.21)$$

and in the second case according to

$$\frac{T_0}{T} = (1 - \eta_C) \qquad (1.22)$$

Theoretically, this is a good definition because Carnot engines are well-defined. Also, energy is well-defined. The important question, of course, is how this definition relates to known temperature scales. We will relate the Carnot temperature scale to the ideal gas temperature scale in the next section.

EFFICIENCY FOR ARBITRARY TEMPERATURES.

We can analyze the general situation for a Carnot engine between arbitrary temperatures as follows. Assume that we have $T > T_0 > T'$, all other cases work similarly. Consider the following couple of Carnot engines (see figure 1.4) and demand that $Q'_1 + Q_2 = 0$ (no heat going in or out the reference system).

Argue that this is equivalent to a single Carnot engine working between T and T'.
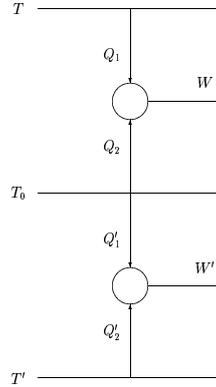
Figure 1.4: **Two Carnot engines in series.**

For this system we have $\frac{T'}{T_0} = (1 - \eta'_C)$ and $\frac{T_0}{T} = (1 - \eta_C)$, or $\frac{T'}{T} = (1 - \eta'_C)(1 - \eta_C)$. The efficiencies can be expressed in the energy exchanges and we have $\frac{T'}{T} = (1 - \frac{W'}{Q'_1})(1 - \frac{W}{Q_1})$. But we have $Q'_1 = -Q_2 = Q_1 - W$ and hence $\frac{T'}{T} = (1 - \frac{W'}{Q_1 - W})(1 - \frac{W}{Q_1})$. The right hand side is equal to $1 - \frac{W}{Q_1} - \frac{W'}{Q_1 - W}(1 - \frac{W}{Q_1}) = 1 - \frac{W}{Q_1} - \frac{W'}{Q_1}$. In other words:

$$\frac{T'}{T} = 1 - \frac{W + W'}{Q_1} = 1 - \eta_C \tag{1.23}$$

where the relation now holds for arbitrary values of the temperature.

Can we obtain negative values of the temperature?

CARNOT CYCLE AGAIN.

Using the temperature scale defined by the Carnot engine, we can reanalyze the Carnot cycle. The efficiency is related to the heat ΔQ_1 absorbed in the first step and ΔQ_2 absorbed in the third step (which is negative in an engine) by

$$\eta_C = 1 + \frac{\Delta Q_2}{\Delta Q_1} \tag{1.24}$$

In other words:

$$\frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} = 0 \tag{1.25}$$

Since there is no heat exchanged in steps two and four of the Carnot cycle, this is equivalent to

$$\oint_C \frac{\bar{d}Q}{T} = 0 \qquad (1.26)$$

where the closed contour C specifies the path of integration in the space of state variables.

INTEGRAL FOR ARBITRARY CYCLES.

Next we consider the combined effect of two Carnot engines, one working between T_1 and T_2, the other one between T_2 and T_3. Now compare this with a single system which follows the thermodynamic transformation defined by the outside of the sum of the two Carnot contours. One can think of the total process as the sum of the two Carnot steps, introducing an intermediate reservoir, in which no net heat is deposited. The contour integral of $\frac{\bar{d}Q}{T}$ is also zero for the single process, since the two contributions over the common line are opposite and cancel. Any general closed path in the space of state variables, restricted to those surfaces which are allowed by the equations of state, can be approximated as the sum of a number of Carnot cycles with temperature difference ΔT. The error in this approximation approaches zero for $\Delta T \to 0$. Hence:

$$\oint_R \frac{\bar{d}Q}{T} = 0 \qquad (1.27)$$

where R is an arbitrary cyclic, reversible process.

DEFINITION OF ENTROPY.

Formula 1.27 has the important consequence that $\int_1^2 \frac{\bar{d}Q}{T}$ is path independent. We define a new variable S by

$$S_2 = S_1 + \int_1^2 \frac{\bar{d}Q}{T} \qquad (1.28)$$

and because the integral is path independent S is a state function. When the integration points are close together we get

$$TdS = \bar{d}Q \qquad (1.29)$$

in which dS is an exact differential. The quantity S is called the entropy. In thermodynamics we define the entropy from a purely macroscopic point of view. It is related to infinitesimally small exchanges of heat energy by requiring that the differential $\bar{d}Q$ can be transformed into an exact differential *by multiplying it with a function of the temperature alone.* One can always transform a differential into an exact differential by multiplying it with a function of all state variables. In fact, there are an infinite number of ways to do this. The restriction that the multiplying factor only depends on temperature uniquely defines this factor,

apart from a constant factor. One could also define $5TdS = \bar{d}Q$, which would simply rescale all temperature values by a factor five.

FIRST LAW IN EXACT DIFFERENTIALS.

The first law of thermodynamics in terms of changes in the entropy is

$$dU = TdS - \bar{d}W \tag{1.30}$$

For example, if we consider a system where the only interactions with the outside world are a possible exchange of heat and mechanical work, changes in the internal energy are related to changes in the entropy and volume through

$$dU = TdS - pdV \tag{1.31}$$

ENTROPY IS EXTENSIVE.

In the definition of the Carnot temperature of an object the size of the object does not play a role, only the fact that the object is in thermal equilibrium. As a consequence the temperature is an intensive quantity. On the other hand, if we compare the heat absorbed by a system during a thermodynamic process with the heat absorbed by a similar system which is α times larger, it is not hard to argue that the amount of heat exchanged is α times larger as well. As a consequence, the entropy S is an <u>extensive state variable</u>.

NATURAL VARIABLES FOR THE INTERNAL ENERGY ARE ALL EXTENSIVE STATE VARIABLES.

Changes in the internal energy U are related to changes in the extensive state variables only, since the amount of work done is determined by changes in extensive state variables only and S is extensive. In this sense, the <u>natural</u> set of variables for the state function U is the set of all extensive variables.

IMPORTANCE OF THERMODYNAMIC LIMIT.

Equation 1.30 has an interesting consequence. Suppose that we decide that another extensive state variable is needed to describe the state of a system. Hence we are adding a term xdX to $\bar{d}W$. This means that the number of internal degrees of freedom is reduced by one, since we are specifying one additional combination of degrees of freedom via X. This in its turn indicates that the entropy should change, since it is a representation of the internal degrees of freedom of the system. The definition of the entropy would therefore depend on the definition of work, which is an unacceptable situation. Fortunately, the thermodynamic limit comes to rescue here. Only when the number of degrees of

freedom is infinitely large, the change by one will not alter the entropy. Hence the entropy is only well-defined in the thermodynamic limit.

INDEPENDENT AND DEPENDENT VARIABLES.

From equation 1.31 we find immediately that

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad (1.32)$$

and

$$p = -\left(\frac{\partial U}{\partial V}\right)_S \qquad (1.33)$$

which shows that in the set of variables p,V,T,S only two are independent. If we know the basic physics of the system, we know the state function $U(S,V)$ and can derive the values for p and T according to the two state functions defined by the partial derivatives. Functions of the form $T = f(S,V)$ and $p = g(S,V)$ are called equations of state. More useful forms eliminate the entropy from these equations and lead to equations of state of the form $p = h(T,V)$. The relation $U = u(S,V)$ is called an energy equation and is not an equation of state, since it defines an energy as a function of the independent state variables. Such relations are the basis for equations of state, but we use equation of state only when we describe state variables that occur in pairs, like T and S, or p and V. Equations of state give dependent state variables of this nature as a function of independent ones.

In the next chapter we will discuss how to change variables and make combinations like T and V independent and the others dependent.

CHANGE IN ENTROPY IN AN IRREVERSIBLE PROCESS.

Up to this point we only considered the entropy in connection with reversible processes. Different rules follow for irreversible processes. Consider a general process in which heat is transferred from a reservoir at high temperature to a reservoir at low temperature (and hence $Q_1 > 0$). The efficiency of this process is at most equal to the Carnot efficiency, and hence

$$\frac{W}{Q_1} = 1 + \frac{Q_2}{Q_1} \leq \eta_C = 1 - \frac{T_2}{T_1} \qquad (1.34)$$

For such a general process we have

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0 \qquad (1.35)$$

Suppose that the heat is taken from the reservoir at high temperature T_1 in a general process, but dumped in the reservoir at low temperature T_2 in a

reversible way. Suppose we only consider small changes in energy. For comparison, consider a completely reversible way of transferring the heat from one reservoir to another. In this process heat is transferred reversibly from the high temperature reservoir to the engine. This leads to

$$\frac{\Delta Q_1^g}{T_1} \leq -\frac{\Delta Q_2^{rev}}{T_2} = \frac{\Delta Q_1^{rev}}{T_1} = \Delta S_1 \qquad (1.36)$$

For a general process at a temperature T, in which the amount of heat added to the system is ΔQ and the change in entropy of the system is ΔS, the changes are related by

$$T\Delta S \geq \Delta Q \qquad (1.37)$$

The equal sign holds for all reversible processes only. Hence in an irreversible process the change in entropy accompanying the absorption of a certain amount of heat is larger than necessary. The change in entropy is minimal for a reversible process. An engine in which all processes are reversible will return to its initial state without a change in entropy. If, however, some processes are not reversible, the entropy of the engine will increase after a complete cycle. It does not return to the same initial state, but to a state of higher entropy. The internal energy of the system decreases more than necessary, and we loose energy, which can be seen from

$$\Delta U = \Delta Q - \Delta W \leq T\Delta S - \Delta W \qquad (1.38)$$

The price in energy we pay to transform a system from one state to another is higher than needed if the transformation is irreversible.

Maximum entropy principle.

If we wait long enough, a completely isolated system will end up in equilibrium. If this system was not in equilibrium to start with, a spontaneous process will take it there. Since the system is completely isolated, there is no exchange of heat with the outside world, and at each time $T\Delta S \geq 0$. In reaching equilibrium by a spontaneous process, the entropy of the system has increased. This is true for any non-equilibrium initial state. Hence we find the following very important rule:

 The equilibrium state of a completely isolated system has maximal entropy.

By completely isolated system we mean that the internal energy U, the volume V, the amount of material N, and all other extensive state variables are kept constant. The way to change the entropy is to change some internal variables, hence the entropy is a maximum as a function of the internal variables only.

This is quite a strong statement based on some minimal input (the second law of thermodynamics).

1.6 Third law of thermodynamics.

Using equation 1.28 we can find the entropy difference between two arbitrary states. This still leaves us with one constant of integration, which could be system dependent. The third law of thermodynamics sets this constant to zero at zero temperature for all systems. The short form of the third law is

$$S(T = 0) = 0 \qquad (1.39)$$

but this is not completely correct. First of all, we cannot reach zero temperature, and second we need to take the thermodynamic limit. Therefore, the correct formulation of the third law is:

$$\lim_{N \to \infty} \lim_{T \to 0} \frac{S(T)}{N} = 0 \qquad (1.40)$$

Note that we cannot interchange the order of the limits, we have to take the limit for the temperature first. This is a general characteristic of the thermodynamic limit, we have to take this limit last, after we have done all our calculations! This is an important point to remember, and a source of errors if done wrong.

RESPONSE AT ZERO TEMPERATURE.

At zero temperature the entropy becomes infinitesimally small compared to the number of degrees of freedom in the thermodynamic limit. In the language of quantum mechanics, the degeneracy of the ground state is very small compared to the number of degrees of freedom. The third law seems to hold for all physical systems. It has an interesting consequence. Suppose we change the state of a system by changing the state variable X, but keep the temperature at zero. Since $S(T = 0, X) = 0$, we find that the partial derivative of S with respect to X has to be 0, or

$$\lim_{N \to \infty} \lim_{T \to 0} \frac{1}{N} \left(\frac{\partial S}{\partial X} \right)_T = 0 \qquad (1.41)$$

This seems to hold for all experiments, and has important consequences for the values of response functions at low values of the temperature.

HEAT CAPACITY AT ZERO TEMPERATURE.

An example of a simple system is a system where the only thermodynamic variables are S, T, p, and V. The internal energy follows from $dU = TdS - pdV$. If we work at constant volume, $dV = 0$, and the first law leads to

$$S(V, T_1) - S(V, T_2) = \int_{T_2}^{T_1} \frac{dU}{T} = \int_{T_2}^{T_1} \frac{dT}{T} \left(\frac{\partial U}{\partial T} \right)_V \tag{1.42}$$

Since according to the third law the left hand side exist for $T_2 \rightarrow 0$, the integral on the right hand side must exist, which implies

$$\lim_{T \rightarrow 0} \left(\frac{\partial U}{\partial T} \right)_V = 0 \tag{1.43}$$

This is also observed experimentally.

T=0 UNREACHABLE.

Another consequence of the third law is the impossibility of reaching $T = 0K$ in a finite number of steps using a reversible process. Problem 7 illustrates this with an example.

1.7   Ideal gas and temperature.

There are several temperature scales used in daily life, like Celcius, Fahrenheit, Reamur, and Kelvin. In thermodynamics we define the temperature first, via an experiment. In statistical mechanics one defines the entropy first (technically such a definition is called an entropy analogue), and derives the temperature from this. Since we cannot measure the entropy directly this is not a good operational definition.

EQUIVALENCY OF TEMPERATURE SCALES.

There are many ways to measure temperature, and experimentally they have all been shown to be equivalent. Therefore, we need only to equate the formal definition of temperature via Carnot engines to one type of measurement in order to show that the Carnot temperature is really the temperature we measure in real experiments.

IDEAL GAS TEMPERATURE.

One standard of temperature is based on the ideal gas. The equations of state for a *monoatomic* ideal gas are

$$U = \frac{3}{2} pV \tag{1.44}$$

and

$$pV = NRT^{id} \tag{1.45}$$

The second equation of state is use to define the ideal gas temperature. If a known amount of an ideal gas is in equilibrium we measure its volume and pressure, and then evaluate the temperature.

IDEAL GAS CANNOT BE AT ZERO TEMPERATURE.

Note that for the ideal gas we have $U = \frac{3}{2}NRT$, and hence $\left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}NR$. This does not approach zero in the limit $T \rightarrow 0$. The ideal gas law $U = \frac{3}{2}pV$ is therefore in contradiction with the third law. The ideal gas law cannot be applied at low temperatures. This is not surprising, since all materials transform to a liquid at sufficiently low temperatures.

CARNOT CYCLE FOR IDEAL GAS.

We now construct a Carnot engine based on an ideal gas. The equations of state show that the internal energy of the ideal gas is determined by the ideal gas temperature only, and hence does not change in an isothermal process. Therefore in steps one and three of the Carnot cycle all the heat absorbed by the system is changed into work. This is not in contradiction with the second law, because in each separate step of a Carnot cycle the system also changes. Note the word "only" in the second law! The Carnot cycle is given by

$$(p_1, V_1, T_1^{id}) \underset{one}{\rightarrow} (p_2, V_2, T_1^{id}) \underset{two}{\rightarrow} (p_3, V_3, T_2^{id}) \underset{three}{\rightarrow} (p_4, V_4, T_2^{id}) \underset{four}{\rightarrow} (p_1, V_1, T_1^{id})$$
(1.46)

During steps one and three the volume and pressure are related via the equation of state, and the first law then states that the work done is equal to the heat absorbed, since the energy is constant:

$$\Delta W_{12} = \Delta Q_{12} = \int_{V_1}^{V_2} pdV = NRT_1^{id} \int_{V_1}^{V_2} \frac{dV}{V} = NRT_1^{id} \ln(\frac{V_2}{V_1}) \qquad (1.47)$$

$$\Delta W_{34} = \Delta Q_{34} = \int_{V_3}^{V_4} pdV = NRT_2^{id} \int_{V_3}^{V_4} \frac{dV}{V} = NRT_2^{id} \ln(\frac{V_4}{V_3}) \qquad (1.48)$$

Steps two and four are adiabatic, and there is no heat exchange. The change in energy is the work done by the system.

$$\Delta W_{23} = \frac{3}{2}NR(T_1^{id} - T_2^{id}) = -\Delta W_{41} \qquad (1.49)$$

$$\Delta Q_{23} = \Delta Q_{41} = 0 \qquad (1.50)$$

We are now able to calculate the efficiency of this engine, which is what we need in order to compare the temperature of the ideal gas with the theoretical temperature. The efficiency is given by:

$$\eta = \frac{\Delta W_{12} + \Delta W_{23} + \Delta W_{34} + \Delta W_{41}}{\Delta Q_{12}} \tag{1.51}$$

which leads to

$$\eta = 1 + \frac{T_2^{id}}{T_1^{id}} \frac{\ln(\frac{V_4}{V_3})}{\ln(\frac{V_2}{V_1})} \tag{1.52}$$

CONNECTING THE ELEMENTS.

In order to analyze this further, we need to calculate the entropy of an ideal gas, which is constant during the adiabatic steps. This will then allow us to connect the values of the volume in states 2 and 3. Using the two equations of state and the first law in terms of the entropy and volume only, we find that small changes in the entropy are related to changes in the temperature and volume by

$$T^{id} dS = \frac{3}{2} d(pV) + p dV = \frac{3}{2} NR dT^{id} + \frac{NRT^{id}}{V} dV \tag{1.53}$$

After dividing both sides by T^{id}, it is not hard to find that one can integrate dS. The entropy for an ideal gas is

$$S(T^{id}, V, N) = NR ln((T^{id})^{\frac{3}{2}} V) + S_0(N) \tag{1.54}$$

Changes in the entropy are related to heat exchange. In an adiabatic process there is no heat exchange, and hence an adiabatic process is a process at constant entropy. In the adiabatic steps two and four of the Carnot cycle changes in the volume are related to changes in the temperature according to

$$\frac{V_3}{V_2} = \left(\frac{T_1^{id}}{T_2^{id}}\right)^{\frac{3}{2}} = \frac{V_4}{V_1} \tag{1.55}$$

which shows that the efficiency is given by

$$\eta = 1 - \frac{T_2^{id}}{T_1^{id}} \tag{1.56}$$

The Carnot temperatures were defined using this efficiency. We have

$$\frac{T_2}{T_1} = 1 - \eta = \frac{T_2^{id}}{T_1^{id}} \tag{1.57}$$

and hence the two temperature scales are proportional to each other. This means that they are really the same, since any temperature scale can always

be modified by a constant scale factor. A similar analysis can be applied to all different kinds of thermometers. Standard thermometers are equivalent to the Carnot scale.

GIBBS PARADOX.

Suppose we have a system with N moles of material in a volume V at temperature T and we add a similar system. If we use 1.54 the total entropy of the combined system is:

$$S_{total}(T^{id}, 2V, 2N) = 2NR\ln((T^{id})^{\frac{3}{2}}V) + 2S_0(N) \qquad (1.58)$$

which has to be equal to

$$S(T^{id}, 2V, 2N) = 2NR\ln((T^{id})^{\frac{3}{2}}2V) + S_0(2N) \qquad (1.59)$$

and hence we need

$$2S_0(N) = S_0(2N) + 2NR\ln(2) \qquad (1.60)$$

which leads to

$$S_0(N) = -NR\ln(N) + NRc \qquad (1.61)$$

where c is some constant. Therefore, the entropy of an ideal gas is

$$S(T^{id}, V, N) = NR\left(ln((T^{id})^{\frac{3}{2}}\frac{V}{N}) + c\right) \qquad (1.62)$$

Hence the dependence of the entropy on N is completely fixed by requiring that the entropy is an extensive quantity. The constant c can be found from statistical mechanical calculations, and the expression for c contains the constant $\hbar$. This is quite remarkable, since this is a direct manifestation of a quantum mechanical quantity in a macroscopic equation!

Without the constant of integration $S_0(N)$ the entropy is not extensive, and using the first part of 1.54 only gives many problems. For example, consider a container of volume V with an amount N_A of material A and a similar container of volume V with an amount N_B of material B, all at temperature T. If we add these containers together, the new entropy is

$$S_{total} = S(T^{id}, 2V, N_A) + S(T^{id}, 2V, N_B) \qquad (1.63)$$

since each gas now occupies twice the volume. The change in entropy is

$$\Delta S = S_{total} - S(T^{id}, V, N_A) - S(T^{id}, V, N_B) =$$

$$S(T^{id}, 2V, N_A) - S(T^{id}, V, N_A) + S(T^{id}, 2V, N_B) - S(T^{id}, V, N_B) \qquad (1.64)$$

which gives

$$\Delta S = (N_A + N_B)Rln(2) \tag{1.65}$$

which is called the entropy of mixing. Therefore, if we mix two different gases the entropy will increase. If we ignore the constant of integration in equation 1.54 we get exactly the same answer if we make the materials A and B the same (Gibbs paradox), which cannot be true, since in this case there should not be a change in entropy. Including the constant of integration resolves this paradox, as we demonstrated when we constructed the analytical form of this constant.

THE FIRST STEAM ENGINE

One can argue about the exact definition of a steam engine, but it is fair to say that Hero already constructed a steam engine more than 2000 years ago. The Romans did not have the analytical methods (mathematics) to analyze this new toy, and never saw any use for it. Can you imagine what would have happened if the Romans, who were masters of engineering, would have had good smooth roads and steam driven cars?

1.8   Extra equations.

1. *How do we measure temperature?*

2. *How large does a thermometer need to be?*

3. *How do we measure pressure?*

4. *What is the difference between direct and indirect measurements?*

5. *Why is characterization in terms of state variables important?*

6. *How realistic are reversible processes?*

7. *What happens when a process is not reversible?*

8. *Comment on time-scales and equilibrium.*

9. *What is the law of large numbers, how does it play a role?*

10. *Would $pV = (NRT)^2$ be a possible equation of state?*

11. *Is pdV an exact differential?*

12. *How is the internal energy defined in thermodynamics?*

13. *Why is the internal energy a state function?*

14. *Why would it be bad is Q and W were state functions?*

15. *How many work terms can there be?*

16. *Why would one treat the μdN term differently?*

17. *Why worry about measuring heat via Carnot engines?*

18. *Why can the efficiency not be greater than one?*

19. *Why is the maximum entropy principle important?*

20. *What is the thermodynamical basis for the maximum entropy principle?*

21. *What is the microscopic basis for the maximum entropy principle?*

22. *Give a possible diagram for an irreversible engine.*

23. *How do we measure entropy?*

24. *How are the laws of thermodynamics obtained?*

25. *Can we reach negative temperatures?*

26. *Would a measure of temperature via T^{-1} be better?*

27. *Give an example of a function where limits cannot be interchanged.*

28. *Explain why we cannot reach T=0 (driving force to zero).*

29. *What is an ideal gas?*

30. *Why is the calculation in sec 1.7 important?*

31. *Using $dU = TdS - pdV$ find the equations of state.*

32. *How many of the variables T,S,p,V are independent?*

33. *Suppose that we have for an ideal gas $pV = NRT$ and $U = Nf(T)$. What are the restrictions on $f(T)$?*

34. *In a p-V-T-S system, suppose I know $T=F(p,V)$, $U=G(p,V)$. Can I find S? Do so.*

1.9 Problems for chapter 1

PROBLEM 1.

A system is characterized by the state variables x and y. The following functions are defined via differential changes in these state variables:

(1) $\bar{d}f = x^2 dx + y^2 dy$

(2) $\bar{d}g = y^2 dx + x^2 dy$

(3) $\bar{d}h = 3x^2y^2dx + (2x^3y + y^4)dy$

For each of these functions f,g, and h determine if they correspond to a state function. Express each state function in terms of x and y.

PROBLEM 2.

The quantity q related to the state variables x and y is defined by $\bar{d}q = xydx + \frac{1}{x}dy$. Show that q is not a state function. The state function s is defined by $ds = f(x)\bar{d}q$ where f is a function of x only. Find f(x)

PROBLEM 3.

The state of a system is determined by the state variables x and y. The actual state of the system can be changed experimentally by changing x and y. The energy U of the system is a function of x and y defined via $dU = \sin(x+y)dx + \sin(x+y)dy$. The work done on the outside world by the system when x and y are changed is given by $\bar{d}W = \sin(x)\cos(y)dx$.

  (a) Show that U is a state function and find U(x,y).

  (b) Show that W is not a state function.

  (c) Give an expression for the differential change in heat $\bar{d}Q$ for this system.

The system is cycled through states (x, y) in a reversible process. The cycle is given by $(0,0) \rightarrow (\alpha\pi, 0) \rightarrow (\alpha\pi, \alpha\pi) \rightarrow (0, \alpha\pi) \rightarrow (0,0)$. α is a parameter with values restricted to $[0, 2]$.

  (d) Calculate the work done on the environment in this cycle and the amount of heat taken up by the system as a function of α.

  (e) For which values of α is this process a heat engine?

PROBLEM 4.

An ideal gas is in equilibrium and has volume V_0, temperature T_0, and pressure p_0. These are the only three state variables we can vary. The amount of material is kept constant at N moles. This gas is cycled through the following process. First it expands at constant pressure to twice the volume. Next, it is cooled at constant volume to half the temperature it had at the beginning of this step. Then its volume is reduced to the original value at constant pressure. Finally, it is heated at constant volume to the original state. During this process an amount of heat $Q_1 > 0$ flows into the system at steps one and four combined, and an amount of heat $Q_2 > 0$ flows out of the system during steps two and three combined. The total amount of work performed on the environment is

W. Calculate the efficiency for this process, defined by the ratio of the work W done on the environment and the amount of heat Q_1 flowing into the system during of the process. Compare this value with the efficiency of a Carnot engine operating between the highest and lowest temperature that occur in the process described above.

PROBLEM 5.

The internal energy of a system as a function of the entropy S and the volume V is given by $U(S, V) = \frac{S^2}{V}$. The only other state variables of importance in this problem are the temperature T and the pressure p.

(a) Using $dU = TdS - pdV$, calculate $p(S, V)$ and $T(S, V)$ for equilibrium states of the system.

(b) Calculate the efficiency of a Carnot cycle for this system as a function of the temperatures of the two reservoirs between which the Carnot engine is operating. Calculate all contributions to the exchange of heat and work, and show that the temperature defined in this problem is indeed equal to the Carnot temperature.

PROBLEM 6.

A magnetic substance has temperature T and magnetization M. The first law in this case is $dU = TdS + HdM$, where H is the applied magnetic field. The internal energy U is a function of T only and does not depend on M, $U = Nf(T)$. The equation of state is $M = \frac{CH}{T}$, where C is a constant proportional to the size of the system. Calculate the efficiency of a Carnot cycle for an engine using a magnetic substance which is doing work on the outside world when reducing the magnetization for this substance, by calculating all contributions to the exchange of heat and work, and show that the temperature defined in this problem is indeed equal to the Carnot temperature.

PROBLEM 7.

This problem is an example of a consequence of the third law: it is impossible to reach absolute zero temperature in a finite number of steps if a reversible process is used. The entropy of a system is given by $S = \alpha VT$, where α is a positive constant and V is the volume of the system. The system is originally at temperature T_0 and volume V_0. A reversible two-step process is used to cool this system. In the first part of the process the system expands adiabatically to a volume $2V_0$. In the second part of the process the system is compressed isothermally back to V_0. Calculate the temperature T_n of the system after this two-step process has been applied n times.

PROBLEM 8.

The internal energy of systems 1 and 2 is given by $U_i = C_i T$, where the constants C_1 and C_2 are both positive. Originally system 1 is at temperature T_1 and system 2 at temperature T_2. These systems are brought into thermal contact. This establishes an infinitesimally slow flow of energy between the systems, but the two systems are completely isolated from the rest of the world and energy cannot flow out of the combined system. The individual systems are always in equilibrium. The total system is not in equilibrium just after contact is established, but finally will reach equilibrium at a common temperature T_f.

(a) Calculate T_f.

(b) Calculate the change in entropy during this spontaneous process.

(c) Show that the entropy did increase.

PROBLEM 9.

A removable partition divides a container in two parts with volumes V_1 and V_2. The container is filled with an ideal gas. The temperature and the pressure in each part are equal to T and p, respectively.

(a) Calculate the amount of material N_1 and N_2 in each part of the system.

(b) Calculate the entropy of the combined system by adding the entropies of the two parts.

The partition is now removed. Since the pressure and temperature of both parts were already equal, the combined system is already in equilibrium.

(c) Calculate the total entropy of the system directly as a function of $N = N_1 + N_2$ and $V = V_1 + V_2$.

(d) Show that the results of b and c are different.

Since the removal of the partition does not cause any spontaneous process, the entropy before and after should be the same. The problem is related to our derivation of the entropy for an ideal gas. The constant S_0 does not depend on T or V, but could still depend on N.

(e) Assuming that S_0 is a function of N, derive its functional form from the requirement that the entropy calculated in b and c is the same.

PROBLEM 10.

An engine operates between a high temperature reservoir and a low temperature reservoir. Everything in this engine is ideal, except that from each amount of heat Q taken by the engine from the high temperature reservoir an amount αQ with $0 < \alpha < 1$ flows at the same time directly into the low temperature reservoir through a leak.

(a) How much entropy is created in this leak?

(b) Calculate the efficiency of this engine.

PROBLEM 11.

A Stirling engine uses the following cycle (all steps are reversible):

(1) Isothermal expansion, absorbing an amount of heat Q_h at T_h.

(2) Isochoric (constant volume) cooling to T_l, giving up an amount of heat Q_c.

(3) Isothermal contraction, giving off an amount of heat Q_l at T_l.

(4) Isochoric warming to T_h, absorbing an amount of heat Q_a.

Using these non-standard definitions all values of Q_i are positive. Assume that $Q_a = Q_c$ and that this energy is recycled, that is the heat given up in step 2 returns to the system in step 4. Show that for an ideal gas the efficiency of the Stirling cycle is less than the Carnot efficiency.

PROBLEM 12.

The temperature is an intensive state variable since the definition is independent of the size of the reservoir. Show that the entropy is extensive, in two different ways, using:

(a) Carnot engines which are working in parallel between the same reservoirs.

(b) the knowledge that the internal energy U is extensive.

PROBLEM 13.

Caratheodory's formulation of the second law is: *There exists arbitrarily close to any given state of a system other states which cannot be reached from it by adiabatic processes alone.* In order to show that this formulation is equivalent to Kelvin's, we use a simple system where only mechanical work can be done. Hence an adiabatic process is described by $dU = -pdV$.

(a) Show that in the U-V plane all points that are connected by adiabatic processes alone define a set of non-intersecting curves.

These curves are labelled by a parameter S, with S(U,V) continuous and differentiable.

(b) Show that **Caratheodory**'s formulation of the second law implies that this is possible

Define $T^{-1} = \left(\frac{\partial S}{\partial U}\right)_V$.

(c) Use the first law to show that identifying S with the entropy and T with temperature is consistent with the standard definitions.

(d) Is the identification in part c the only possible one?

PROBLEM 14.

An ideal gas is defined by the equations of state $pV = NRT$, $U = \frac{3}{2}NRT$, and $S = NR\ln(T\sqrt{T}\frac{V}{N})$. It is used in an engine following the Otto cycle:

(1) Adiabatic compression from volume V_1 to a smaller volume V_2, with temperature changing from T_c to T'.

(2) Heating at constant volume to a temperature T_h.

(3) Adiabatic expansion $V_2 \rightarrow V_1$ (power stroke). The temperature changes to T''.

(4) Cooling at constant volume to T_c.

The amount of heat absorbed by the gas in step two is Q_{in}, the amount of heat absorbed by the gas in step four is Q_{out} (which is negative). Calculate the efficiency of the Otto cycle and show that it is less than the efficiency of a Carnot cycle operating between T_h and T_c.

PROBLEM 15.

In this problem we use $dS = \frac{1}{T}dU + \frac{p}{T}dV$. The internal energy is given by $U(T,V) = cVT^4$, with c a constant. Since the entropy is a state function, dS is exact. Use this to show that $p(T,V) = \frac{1}{3}cT^4 + f(V)T$, where $f(V)$ is a function of volume only. Calculate the entropy $S(T,V)$ and show that $f(V) \equiv 0$.

PROBLEM 16.

Consider the following differential:

$$\bar{d}f = g(x,y,z)dx + h(x,y,z)dy + k(x,y,z)dz$$

What are the necessary and sufficient conditions for $\bar{d}f$ to be exact?

PROBLEM 17.

Consider the following examples:

$$\bar{d}f = 3x^2y^2zdx + 2x^3yzdy + 6x^3y^2dz$$

$$\bar{d}g = 2xy^2z^2dx + 2x^2yz^2dy + 2x^2y^2zdz$$

Are these differentials exact? If so, find the corresponding state function.

PROBLEM 18.

A system is completely described by the four state variables T,S,p, and V.

1. Show that the general form of the energy equation is $U = Vf(\frac{S}{V})$.

2. If $U = S^\alpha V^{1-\alpha}$ find the equations of state p(S,V) and T (S,V).

3. The entropy S is not always easy to deal with, and we often eliminate this variable. In the previous case, solve for p(T,V). What is special in this equation, and why is that the case?

4. Calculate the efficiency of a Carnot engine using a material with the energy equation $U = S^\alpha V^{1-\alpha}$.

PROBLEM 19.

Consider the following cyclic process (Brayton), with an ideal mono-atomic gas as the working material :

1. Adiabatic expansion from p_A, V_1, T_1 to p_B, V_2, T_2.

2. Isobaric expansion from p_B, V_2, T_2 to p_B, V_3, T_3.

3. Adiabatic contraction from p_B, V_3, T_3 to p_A, V_4, T_4.

4. Isobaric contraction from p_A, V_4, T_4 to p_A, V_1, T_1.

Calculate the efficiency in terms of p_A and p_B. Compare this with the Carnot efficiency (indicate the temperatures used, and why you choose these references).

Chapter 2

Thermodynamic potentials and response functions.

2.1 Internal energy.

POTENTIAL ENERGY.

When a mass is dropped from a certain height, it will gain kinetic energy. If it hits the floor, this kinetic energy will be transformed into heat and/or do work. The amount of work this mass is able to do is completely determined by the difference in potential energy between the initial position and the floor. Hence the gravitational potential energy is a measure of the amount of energy stored in this mass initially, which energy can be released to do work.

ENERGY STORED IN A GAS.

Energy is also stored in a gas. If we allow a gas to expand, it will do work on the outside world. The amount of energy which can be released, however, depends on the nature of the process by which the gas is doing this work. In most cases some of the thermodynamic variables are kept constant. A standard example is the expansion of a gas at constant temperature or pressure. The energy which can be released depends on the values of these constant variables. For each situation one defines an appropriate thermodynamic potential or free energy. This makes thermodynamics slightly more complicated than ordinary mechanics. One has to remember which thermodynamic potential applies in which case.

Why does the energy given up by a gas depend on the process?

Internal energy is a free energy.

The easiest thermodynamic potential pertains to a process which is adiabatic. In an adiabatic process there is no heat exchange and the entropy is constant. The first law is in this case $\Delta U = -\Delta W$. In other words:

The internal energy measures the amount of work a system is able to do in an reversible adiabatic process.

This tells us that the internal energy is the appropriate thermodynamic potential or <u>free energy</u> for an adiabatic process. As usual, in reality the amount of work done is always less then the change in internal energy due to inefficiencies in the process. But those details are of a technical nature, and can be minimized by improving the design.

Internal energy and extensive state variables.

Consider a completely isolated or closed system. All the extensive variables of the system have either a fixed value or interact with a generalized external force which is zero. In a closed system the amount of material N is constant and typically the volume V is constant. We might, however, not be able to set all extensive state variables. For example, the magnetic moment $\vec{M}$ might freely find its optimal value. This is only true if the external magnetic fields are small enough. If that is the case, the magnetic moment is an unimportant state variable and we ignore it in the description of the system. One only includes state variables which can be measured, and if there are no external magnetic fields we cannot measure the magnetic moment. One has to include the entropy though. Since the system cannot exchange heat with the outside world, the entropy is constant, but its actual value will determine the value of the internal energy. In our closed system at constant volume and number of particles the internal energy is a function of the entropy, the volume, and the amount of material only, *when the system is in equilibrium.* Hence we have U(S,V,N). Also, the temperature T and the pressure p, and the chemical potential μ are completely determined by the values of S, V, and N. The natural set of state variables to describe a completely isolated system are all the extensive state variables which cannot be changed without doing work on the outside world. The free energy for such a system is the internal energy.

Minimum energy principle.

The number of parameters to describe a macroscopic system is infinitely large. We could decide to measure some of those by using an appropriate external probe. For example, we could divide the total system in two parts, separated by a movable wall (no friction), which is an ideal thermal conductor.
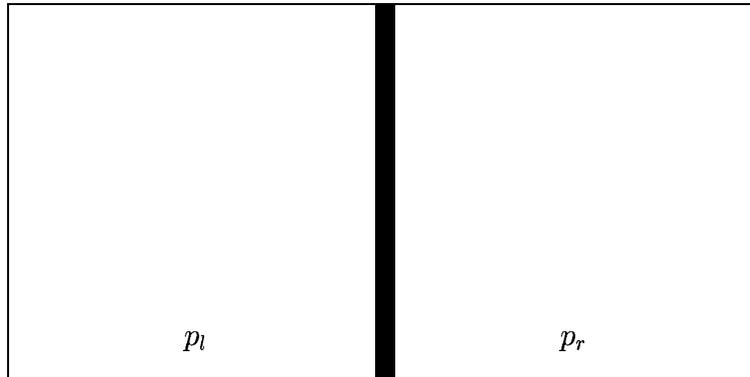
Figure 2.1: **Container with piston as internal divider.**

The pressure in the left part is p_l and in the right part p_r. Assume that the left and right part of the system are both in equilibrium, but not necessarily with each other. The parameter p_l is an additional parameter needed to describe this system. This is a macroscopic parameter, since it pertains to a macroscopic part of the system. Once we know p_l, we know V_l (equilibrium) and hence V_r and p_r. In equilibrium we obviously need $p_l = p_r$ (no net force on the partition), otherwise the wall would move. Suppose the system is not in equilibrium, however, and that $p_l < p_r$. The opposite case can be treated in a similar way.

No friction.

First assume that this is the complete system, and that there is no friction. It is easy to see what will happen. The wall will start to move to the left, and gain kinetic energy. At the point where $p_l = p_r$ the wall is moving, and will keep moving to the left until the pressure on the left is what the original pressure was on the right. Then the process will continue in reverse. The wall will oscillate! Since there is no exchange with the outside world and since there is no friction, for the complete system we have $\Delta V = \Delta N = \Delta S = 0$ and indeed the internal energy does not change.

With friction.

In the second case suppose there is friction and the wall looses energy to the gas when it is moving. The wall will again oscillate, but now this oscillation is damped, and the final state has the wall at a position with $p_l = p_r$. The
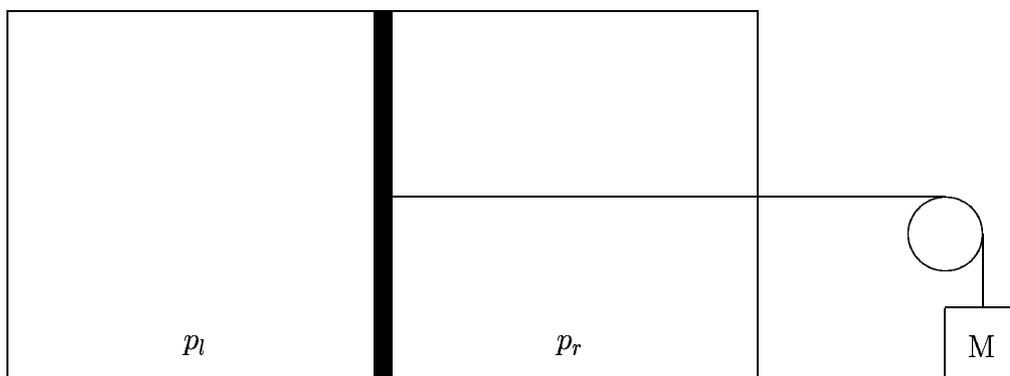
Figure 2.2: **Container where the internal degree of freedom becomes external and hence can do work.**

mechanical energy of the partition has been transformed into thermal energy of the gases! Since the whole system is isolated we have $\Delta Q = 0$ and hence for this process we find from 1.37 $\Delta S \geq 0$. This agrees with the maximum entropy principle, the equilibrium state corresponds to maximum entropy as far as the internal coordinates are concerned.

WALL CORRESPONDS TO STATE VARIABLE.

In the third case we connect the movable wall with a massless cord to some object with mass M (see figure). The value of this mass M is adjusted in such a way that $Mg = (p_r - p_l)A(1 - \epsilon)$ is always true, where A is the area of the movable wall. We also take the limit $\epsilon \to 0$, which allows the wall to move in a quasi-static manner. Therefore, in this system there is no net force acting on the wall, or the generalized force connected with the state variable corresponding to the wall position is always zero. We also assume that there is no friction.

At this point the total system is in equilibrium. Now we make the mass M smaller by very slowly taking very small pieces of that mass away. At every point during this process the total system is in equilibrium, and the whole process is reversible. The wall will move slowly to the left, and the mass M will move upwards. Hence the system is doing work on this mass. At the end, the mass is zero and the wall does not interact with the outside any more. The total system is in equilibrium, as is the closed system itself.

In this process there is always equilibrium and because the wall is a thermal conductor we always have $T_l = T_r$. Since there is no heat exchange with the outside world we have $T_l \Delta S_l = \Delta Q_l = -\Delta Q_r = -T_r \Delta S_r$, and hence $\Delta S_l = -\Delta S_r$. For the total system we have therefore $\Delta S = 0$, as it should be for a reversible process.

Originally, the closed system was not in equilibrium. The internal energy of

the original system was higher than in the final equilibrium situation, since during the process of reaching equilibrium mass was lifted to a higher gravitational potential energy. The internal energy of the system is now lower. We arrive at the important conclusion:

The internal energy of a closed system is a minimum as a function of all parameters which are not fixed by external constraints.

Explain carefully the difference between these three scenarios.

FORMAL DERIVATION OF MINIMUM ENERGY PRINCIPLE.

This minimum energy statement also follows from the relation between energy, entropy, and work, $T\Delta S \geq \Delta U + \Delta W$. In our example of case three we have a closed system, and the parameters S, V, and N are fixed, but the internal coordinate p_l is allowed to vary. No work is done on the outside world by changing the extensive parameters V and N, and neither is heat exchanged, which keeps S constant. Hence for a spontaneous process bringing us from the initial non-equilibrium situation to the final equilibrium situation, we have $0 \geq \Delta U + 0$. The internal energy decreases and is minimal at equilibrium. Note that this minimum principle does not hold for those variables which are fixed by non-zero external constraints, since a change in those variables involves work done on the outside world and the nature of the outside world has to be taken into account.

If a system is kept at constant entropy, volume, etc, it will still be able to exchange energy with the outside world. In the earlier thought experiment we had one of the internal degrees of freedom do work. In general, that is not possible. But a system at constant entropy is still able to exchange heat with the outside world! The loss in internal energy is due to heat dumped to the outside world. Remember, that only for reversible processes we have $T\Delta S = \Delta Q$. If a system spontaneously goes to equilibrium, the process is by definition irreversible.

DIFFERENCE BETWEEN MINIMUM ENERGY AND MAXIMUM ENTROPY.

In the previous chapter we considered a system at constant *energy*, volume, amount of material, etc. All the extensive variables that would be able to do work are kept constant, and hence no work is done. The internal energy is also constant, and hence no heat is transferred either. We want to find the entropy. Suppose we have a model that allows us to calculate $S(U, V, N, X_{int})$ where X_{int} represents the internal degrees of freedom. The maximum entropy principle tells

us that we can find the values of these internal coordinates (coordinates that are not connected to terms in the work differential) by maximizing the function S. In the current chapter we consider a system at constant *entropy*, volume, amount of material, etc. In this case there is again no work done, but heat can be exchanged. Suppose we now have a model that allows us to calculate $U(S, V, N, X_{int})$. The minimum energy principle tells us that we can find the values of these internal coordinates.

EXAMPLE.

A typical application of this minimum principle would be the determination of the magnetic moment of a gas. Consider the variable $\vec{M}$ as an internal parameter. A typical form of the internal energy of a gas with magnetic moment $\vec{M}$ would be $U(S, V, N; \vec{M}) = U(S, V, N; \vec{0}) + \frac{1}{2V}M^2$. The last term represents the self-energy needed to create a magnetic moment. The minimum principle tell us that the magnetic moment has to be zero in equilibrium in this case. Additional interactions are needed to create a magnetic moment, like applying a non-zero magnetic field.

INTERNAL ENERGY AND ADIABATIC PROCESSES.

The internal energy measures the amount of work a system can do in an adiabatic process. Consider a thermally isolated system which can change its volume by expanding. An example is a gas in an completely insulated cylinder with a piston. The system starts in equilibrium with the piston fixed by an external force. In the next step, the piston is allowed to move and work is performed on the outside world. The piston stops again, and the volume of the system is increased. Is the amount of work done equal to the change in internal energy? The answer is no, since the final state might not be in equilibrium. If the final state is not in equilibrium, its value of the internal energy is too high, and hence the amount of work done is less than expected! The final state will go to equilibrium, but since the piston is now fixed, there is no mechanical contact with the outside world anymore. The only way to get rid of the excess energy is to dump heat into the outside world. The internal energy measures the amount of work a system can do in a reversible, adiabatic process. The amount of work done in an irreversible process, starting from an initial state in equilibrium, is always less, because heat is generated. If we assume that the outside world is always in thermal equilibrium, this indicates that the entropy of the outside world must increase.

The irreversible expansion is described in two steps. We start at volume V_i and entropy S_i, with the system in equilibrium and $U_i = U(S_i, V_i, N)$. Next, the system expands to a volume V_f and entropy S_f. The amount of work done is ΔW. The system is not in equilibrium, however, and the internal energy is NOT equal to $U(S_f, V_f, N)$, but is equal to $U_i - \Delta W$. The system now follows a spontaneous process and reaches equilibrium. This is a process at

constant S and V, and in the end the energy is $U_f = U(S_f, V_f, N)$. The change in energy is $\Delta U = U_f - U_i$. The value of ΔW depends on the nature of the irreversible process, and is in general hard to calculate. We only know for sure that $U_i - \Delta W \geq U_f$ or $\Delta W \leq -\Delta U$. Note that the change in entropy is hard to predict, since we have in general no formulas to describe non-equilibrium states. It will depend on the changes in the temperature in the second step. Our final conclusion is that:

The internal energy measures the amount of work a system is able to do in an reversible adiabatic process. It gives an upper-bound for the amount of work done in irreversible processes.

2.2 Free energies.

THE PROBLEM OF HAVING TOO MANY VARIABLES.

The thermodynamic potential governing the adiabatic expansion of a gas is the internal energy. Other measures of the free energy are needed in different types of processes. What do we need when the system is able to exchange heat or particles with the outside world? In other words, which variables are controlled? Do we keep the volume or pressure constant?

A construction of the appropriate free energy is straightforward, and will be illustrated via an example system. Suppose the only extensive state variables which we can measure or change are the volume V and the amount of material N. The work done in such changes depends on the pressure p and the chemical potential μ. We can write

$$\bar{d}W = pdV - \mu dN \tag{2.1}$$

Note again the difference is sign between the mechanical work term and all others. In this formula for the work done we always see a combination of the differential of an extensive variable and the corresponding intensive variable. How can we change that to the product of an extensive variable and the differential of the corresponding intensive state variable? The answer is found by considering the product of corresponding extensive and intensive state variables. The differential of such a product is easy to calculate, since $d(xy) = xdy + ydx$. This suggests that we have to add to or subtract from the internal energy terms of the form pV and μN. Such transformations are called Legendre transformations.

HELMHOLTZ FREE ENERGY.

As a first example we consider the Helmholtz free energy

$$F = U - TS \qquad (2.2)$$

By definition, F is a state function and its differential is exact. Note that some books use the notation A for the Helmholtz free energy. The combination TS is a mixture of an intensive variable, T, and an extensive variable, S. A small change in the Helmholtz energy is related to changes in heat and work via the first law:

$$dF = dU - d(TS) = \left(\bar{d}Q - TdS\right) - SdT - \bar{d}W \qquad (2.3)$$

In a reversible process $\bar{d}Q - TdS = 0$, and now the interpretation of the formula for dF is easy. If we consider a thermodynamic process at constant temperature, the amount of work done on the outside world is equal to the decrease in Helmholtz free energy. Hence:

The Helmholtz free energy measures the amount of work a system can do in an isothermal, reversible process!

If a process is not reversible, the first term in 2.3 does not vanish. For an irreversible process we have $\bar{d}Q < TdS$ and hence for an irreversible isothermal process $dF < -\bar{d}W$. Hence, like in the case of the internal energy, the Helmholtz free energy measures the maximal amount of work a system can do in an isothermal process. In order to do this maximal amount of work, the process has to be reversible. In addition, for a spontaneous process in which no work is done, $dF < 0$. Hence we arrive at the following minimum principle:

The Helmholtz free energy of a system at constant temperature is a minimum as a function of all parameters which are not fixed by external constraints.

Again, this is very similar to the minimum principle for the internal energy. The big difference is that we are now considering a process in which we keep the temperature constant. This requires in general that the entropy has to change, which means that heat will flow. Therefore, the amount of work that can be done is different than that can be done at constant entropy!

NATURAL VARIABLES.

The change in Helmholtz free energy in a *reversible* process is given by

$$dF = -SdT - pdV + \mu dN \qquad (2.4)$$

for a system which interacts with the outside world through heat exchange (dT), mechanical work (dV), and chemical work (dN). This form suggests that the <u>natural variables</u> for an expression of the Helmholtz free energy are T, V,

and N. Similarly, for the internal energy U the natural variables are S, V, and N.

Why are natural variables more useful than other combinations?

OTHER FREE ENERGIES.

Using the idea of Legendre transformations many more free energies can be constructed. Three very useful forms are:

$$\underline{Gibbs\ potential} \quad G = U - TS + pV \tag{2.5}$$

$$\underline{Enthalpy} \quad H = U + pV \tag{2.6}$$

$$\underline{Grand\ potential} \quad \Omega = U - TS - \mu N \tag{2.7}$$

All these potentials are state functions and their differentials are all exact. The Gibbs potential measures the amount of work a system can do at constant temperature and pressure. Since we work at constant pressure, the volume has to change and our system will do mechanical work on the outside world. This amount of energy cannot be used, because it is needed to keep the pressure constant. Similarly, the system is kept at constant temperature and heat will flow to the outside world. Again, this is energy which cannot be used. Hence the Gibbs potential measures the amount of non-mechanical (not-pdV) work a system can do on the outside world at constant pressure and temperature. If μdN is the only other term in the expression for $\bar{d}W$, then the Gibbs free energy is a measure of the amount of chemical work a system is able to do.

The enthalpy measures the amount of work a system can do in an adiabatic, isobaric process. Again, this is the amount of non-mechanical work, since the pressure has to be kept constant. The grand potential pertains to processes at constant temperature and chemical potential. Therefore, it measures non-chemical work, and in a simple system this is only mechanical, pdV type of work. The Gibbs potential and the enthalpy are typically used to describe solids, where one cannot change the volume directly but only through changes in the pressure. The grand potential is useful in chemistry, where the number of particles can change due to chemical reactions and where this number can only be determined by specifying the chemical potential. All these potentials obey a minimum principle similar to those we saw before.

SUMMARY OF FIVE FREE ENERGIES.

In summary, we introduced five free energies (others can be constructed in a similar manner):

Symbol	Differential (reversible)	Natural variables	Name
U	$dU = TdS - pdV + \mu dN$	S,V,N	Internal energy
$F = U - TS$	$dF = -SdT - pdV + \mu dN$	T,V,N	Helmholtz free energy
$G = F + pV$	$dG = -SdT + Vdp + \mu dN$	T,p,N	Gibbs free energy
$H = U + pV$	$dH = TdS + Vdp + \mu dN$	S,p,N	Enthalpy
$\Omega = F - \mu N$	$d\Omega = -SdT - pdV - Nd\mu$	T,V,μ	Grand potential

The internal energy is the only free energy which is expressed in changes of extensive variables only. All the other energies involve at least one intensive variable. If we prescribe a given set of natural variables, the equilibrium state of a system can be found by minimizing the appropriate free energy as a function of all internal variables. Which set of <u>natural variables</u> we use depends on the system we want to describe.

In a given experiment, independent state variables are those variables whose values we can control. This can mean two things. First, it could be that we are able to set the value of the variable at any value we want (often in a certain range only, though). For example, if we have a container with a piston we can set the volume of the container at arbitrary values by fixing the position of the piston. A more common way of controlling a state variable, however, is to prevent its value from changing! A gas in a closed container has a fixed volume. Any state variable which we can control by either setting its value or by preventing changes in its value is an independent variable. These independent variables are the variables we select as natural variables.

Is it possible to write $H(T,V,N)$?

GENERAL FORMALISM.

The general form for the differential of the internal energy is

$$dU = TdS + \sum_j x_j dX_j \qquad (2.8)$$

which follows from 1.17. A general Legendre transformation pertaining to an adiabatic environment would single out the values of j included in a set $\mathcal{J}$ and define

$$Y_{\mathcal{J}} = U - \sum_{j \in \mathcal{J}} X_j x_j \qquad (2.9)$$

with a corresponding differential

$$dY_{\mathcal{J}} = TdS - \sum_{j \in \mathcal{J}} X_j dx_j + \sum_{j \notin \mathcal{J}} x_j dX_j \qquad (2.10)$$

In order to change to the temperature as a natural variable we also subtract a term TS. A typical example might be the discussion of magnetism in a solid. We have no way to fix the total magnetic moment $\vec{M}$ other than using a magnetic field $\vec{H}$. Therefore, $\vec{H}$ is the natural variable for this system, and typically we use a Gibbs-like energy $\mathcal{G}$, defined by $\mathcal{G} = U - TS + pV - \vec{M} \cdot \vec{H}$, to describe this system. The differential for $\mathcal{G}$ is $d\mathcal{G} = -SdT + Vdp + \mu dN - \vec{M} \cdot d\vec{H}$.

2.3 Euler and Gibbs-Duhem relations.

SCALING OF THE INTERNAL ENERGY.

Changes in the internal energy are related to changes in the extensive variables, and the set of all extensive variables is the natural set of variables to describe U. In a general case we have $U(S, V, N, X)$ where X represents all other extensive variables which can be measured and specified to determine the nature of the system. If we consider a homogeneous system, in which all extensive variables are scaled by a value λ, we can derive the following relation:

$$U(\lambda S, \lambda V, \lambda N, \lambda X) = \lambda U(S, V, N, X) \tag{2.11}$$

This holds for all values of λ! This relation can be differentiated with respect to λ. The result involves partial derivatives of U, and since we have so many choices for our independent variables, we will always specify the constant variables in the partial derivatives. We find

$$\left(\frac{\partial U}{\partial S}\right)_{V,N,X} S + \left(\frac{\partial U}{\partial V}\right)_{S,N,X} V + \left(\frac{\partial U}{\partial N}\right)_{S,V,X} N + \left(\frac{\partial U}{\partial X}\right)_{S,V,N} X = U \tag{2.12}$$

where we have set λ equal to one.

Since the partial derivatives involve the natural state variables for U, they can be obtained from the differential for U:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N,X} = T \tag{2.13}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N,X} = -p \tag{2.14}$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,V,X} = \mu \tag{2.15}$$

$$\left(\frac{\partial U}{\partial X}\right)_{S,V,N} = x \tag{2.16}$$

where x is the generalized force corresponding to X. Therefore we find the important relation (Euler equation)

$$U = TS - pV + \mu N + xX \qquad (2.17)$$

The other free energies obey similar relations, which can be derived immediately from this expression. For example, the Gibbs energy for a system which can only exchange heat, do mechanical work (pdV) and chemical work (μdN) is $G = \mu N$. This is a very simple expression indeed. In such a case it is often easier to work with the chemical potential then with the Gibbs energy itself. Note that expression 2.17 implies that we work in the thermodynamic limit. We need the freedom to choose x in 2.17 in an appropriate way. This choice should not change the definition of S, and hence the number of internal degrees of freedom should be very large. In that case a change in the number of internal degrees of freedom by a few does not matter.

INDEPENDENT VARIABLES.

Equations 2.13 through 2.16 show that for a system in equilibrium the values of the temperature, pressure, etc are completely determined once we specify all the extensive state variables. In general, the set of state variables $\{S, T, p, V, \mu, N, X, x\}$ contains only four independent variables. The physics of the system is completely determined by the relation U(S,V,N,X) and everything else follows. Obviously, we can change variables if we want. For example, we could use $\{T, V, N, X\}$ as independent variables. The natural energy to determine in this case is the Helmholtz free energy F. The partial derivatives of F with respect to $\{T, V, N, X\}$ are straightforward and easy to obtain from the expression for the differential of F. Since we switch variables so often, we always want to add the constants to the notation of the partial derivatives.

NOT ALL INTENSIVE VARIABLES ARE INDEPENDENT.

The differential for dU is related to the changes in all extensive variables. If we take the differential of 2.17 we also find terms pertaining to changes in the intensive variables. These additional terms have to sum to zero, and hence

$$SdT - Vdp + Nd\mu + Xdx = 0 \qquad (2.18)$$

This is called the Gibbs-Duhem relation. In words, not all changes in the intensive variables are independent. This means that if we change basic variables in the set $\{S, T, p, V, \mu, N, X, x\}$ it is not possible to choose $\{T, p, \mu, x\}$ as our set of independent variables. Every other choice is allowed, though. It is not hard to understand this restriction. The intensive variables are independent of the size of the system, and cannot specify the size of the system. We need at least one measure of how large the system is. If all intensive variables were independent, we could, however, choose them as a basic set of state variables, which is in contradiction with the previous sentence.

FORMULATION IN TERMS OF DENSITIES.

Another way of looking at the dependency of the intensive variables is working with densities in stead of extensive variables. For example, we could specify the energy per unit volume or per particle. If we define all extensive variables per unit volume

$$s = \frac{S}{V}, u = \frac{U}{V}, n = \frac{N}{V}, \mathcal{X} = \frac{X}{V} \tag{2.19}$$

we find

$$u = Ts + \mu n + x\mathcal{X} \tag{2.20}$$

and using $V\,du + u\,dV = d(uV) = dU = T d(sV) - p\,dV + \mu d(nV) + x d(\mathcal{X}V)$, which is equal to $(Ts - p + \mu n + x\mathcal{X})\,dV + (Tds + \mu dn + xd\mathcal{X})\,V$, we derive

$$du = Tds + \mu dn + xd\mathcal{X} \tag{2.21}$$

Similar formulas hold for densities per particle or other combinations. Hence one of the extensive variables can always be scaled out, and does not contribute to the basic physics of the system. It merely sets the size and is, of course, needed in that respect.

USING A LEGENDRE TRANSFORMATION.

Yet another way of looking at this problem is to define the following free energy via a Legendre transformation:

$$Y = U - TS - \mu N - xX = -pV \tag{2.22}$$

The free energy Y is a state function and an extensive quantity. Its natural variables are $\{T, \mu, x, V\}$. Hence we have

$$Y(T, \mu, x, V) = -Vp(T, \mu, x, V) \tag{2.23}$$

If we scale the volume to αV and use the extensive nature of Y, we find

$$p(T, \mu, x, \alpha V) = p(T, \mu, x, V) \tag{2.24}$$

for all values of α. If we now take the limit $\alpha \to 0$, we see that the pressure does not depend on the volume, and that it is a function of the other intensive variables only.

2.4   Maxwell relations.

Basic principle.

One should not memorize Maxwell relations, but in stead recognize the basic principle which determines all these relations. If a function of many variables is twice differentiable, and if the second order derivatives are continuous, the order in which we take the second order derivatives is not important. We apply this rule to all possible free energies and all possible combinations of independent variables. This yields a large number of relations, called Maxwell relations. The most important occur when we take each free energy as a function of its natural variables, since in that case the first order derivatives are simple state variables. These simple state variables can be found immediately by inspecting the form of the differential. Since so many combinations of state variables are possible, we always write the constant state variables in the notation of the partial derivatives.

Simple example.

As an example consider F(T,V,N), with $dF = -SdT - pdV + \mu dN$. There are three choices for the mixed second order derivatives, leading to the three Maxwell equations:

$$\left(\frac{\partial^2 F}{\partial T \partial V} \right)_N = -\left(\frac{\partial S}{\partial V} \right)_{T,N} = -\left(\frac{\partial p}{\partial T} \right)_{V,N} \tag{2.25}$$

$$\left(\frac{\partial^2 F}{\partial T \partial N} \right)_V = -\left(\frac{\partial S}{\partial N} \right)_{T,V} = \left(\frac{\partial \mu}{\partial T} \right)_{V,N} \tag{2.26}$$

$$\left(\frac{\partial^2 F}{\partial N \partial V} \right)_T = \left(\frac{\partial \mu}{\partial V} \right)_{N,T} = -\left(\frac{\partial p}{\partial N} \right)_{V,T} \tag{2.27}$$

These relations are very important, since they connect changes in one state variables to changes in another state variable in a different process. They limit the freedom of a system in equilibrium to respond to external causes. Maxwell relations are easy to derive if you know which state variables are your basic set, which free energy belongs to that set, and which form the differential has.

Which relations to use?

It is not hard to find out if a Maxwell relation can be found, as long as we use the convention of indicating all variables that are kept constant. For example, consider the derivative $\left(\frac{\partial p}{\partial S} \right)_{N,V}$. The set of variables used is $\{S, N, V\}$ and this is indeed the set of natural variables for a free energy, in this case the internal

energy U. In general, we have a good set of variables if from each pair $\{T, S\}$, $\{p, V\}$, $\{\mu, N\}$, and $\{x, X\}$ exactly one variable is used.

The variable which is differentiated is one of the remaining variables (else the derivative is trivial), and can be found by inspecting the differential of the free energy for which the set of variables is the set of natural variables. In our example we have $p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$ and hence

$$\left(\frac{\partial p}{\partial S}\right)_{N,V} = -\left(\frac{\partial^2 U}{\partial V \partial S}\right)_N = -\left(\frac{\partial T}{\partial V}\right)_{N,S} \tag{2.28}$$

2.5   Response functions.

Linear response.

How do we investigate the physics of some system? How do we perform a basic measurement? We apply an external field, and measure the response of the system. For example, we change the temperature of a metal rod and measure the change in length. Life would be simple, and thermodynamics easy, if all responses were linear. This is not true, unfortunately. A linear relation between cause and effect is only true in the limit of small changes of the causing agents, when we can write

$$\Delta A = \left(\frac{\partial A}{\partial B}\right)_{C,D,..} \Delta B \tag{2.29}$$

for a change in B, keeping C,D,... constant. We do not know how small ΔB has to be in order for a linear relation to be a good approximation. Ohm's law holds for metals for large changes in the applied voltage, but for semiconductors the linear range is very small. If we measure the magnetic susceptibility of iron, a change in temperature of 1K at room temperature is small, because the Curie temperature of iron is very large. Near the Curie point, however, changes are more rapid since some of the derivatives start to diverge.

When is a linear approximation to the response of a system good enough?

The linear relation 2.29 holds for small changes in B, and by measuring A we can find the partial derivative. Since the partial derivative measures the response in A of the system to a small change in B, it is called a <u>response function</u>. The most important way we obtain information about thermodynamic systems is by measuring response functions. Hence measurements give us response functions, and the analysis of the behavior of response functions then will allow us to draw conclusions about the physics of the system!

Heat capacities.

Heat capacities are one of the most important thermodynamic response functions to measure. The tell us how much heat the system will take up if we increase its temperature. These measurements are always performed as a function of temperature, but can be done either at fixed pressure or volume. The other *extensive* thermodynamic variables kept constant are denoted by X. Hence we have

$$C_V(T, V, X) = \left(\frac{\Delta Q}{\Delta T} \right)_{V,X} = T \left(\frac{\partial S}{\partial T} \right)_{V,X} \tag{2.30}$$

$$C_p(T, p, X) = \left(\frac{\Delta Q}{\Delta T} \right)_{p,X} = T \left(\frac{\partial S}{\partial T} \right)_{p,X} \tag{2.31}$$

The heat capacities are related to the partial derivatives of the entropy, since the entropy governs heat exchange. The heat capacity at constant volume is directly related to the internal energy. Since we know that for small changes $\Delta U = T\Delta S - p\Delta V + x\Delta X$, we can write for a process in which the temperature changes by a small amount ΔT, but the volume V and the variables X are kept constant,

$$\frac{\Delta U}{\Delta T} \bigg|_{V,X} = T \frac{\Delta S}{\Delta T} \bigg|_{V,X} \tag{2.32}$$

In the limit $\Delta T \to 0$ the ratios become partial derivatives, and we have

$$C_V(T, V, X) = \left(\frac{\partial U}{\partial T} \right)_{V,X} \tag{2.33}$$

Similarly, for a process at constant pressure and X, the differential of U yields

$$\frac{\Delta U}{\Delta T} \bigg|_{p,X} = T \frac{\Delta S}{\Delta T} \bigg|_{p,X} - p \frac{\Delta V}{\Delta T} \bigg|_{p,X} \tag{2.34}$$

and hence

$$C_p(T, p, X) = \left(\frac{\partial U}{\partial T} \right)_{p,X} + p \left(\frac{\partial V}{\partial T} \right)_{p,X} \tag{2.35}$$

Since most materials expand when heated, the volume change in the last case will cause the system to do work and we have to supply this energy. We expect therefore $C_p > C_V$. Also, in general we need heat to increase the temperature, so we also expect $C_V > 0$. These statements will be proven later in the this chapter, where we talk about equilibrium conditions. Heat capacities are extensive state functions. One often defines a specific heat by using the heat capacity per unit volume or per unit mass. Unfortunately, the word specific heat is used for both

these ratios, so make sure that you understand from the context of the problem which one applies.

COMPRESSIBILITIES.

Another set of response functions which are often measured are related to volume changes, and called compressibilities. We apply pressure to a system and measure the change in volume. A measurement like this is done either adiabatically or isothermally, and the two relevant compressibilities are

$$\kappa_T(T, p, X) = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,X} \tag{2.36}$$

$$\kappa_S(S, p, X) = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{S,X} \tag{2.37}$$

We expect $\kappa_T > \kappa_S > 0$ because at constant entropy the internal variables of the system are essentially only scaled to a smaller volume, but at constant temperature they can also rearrange to allow for an even smaller volume. Again, these inequalities follow from the equilibrium conditions later in the this chapter. The minus sign is included to indicate that the volume decreases with increasing pressure. The size of the system is scaled out by dividing by the volume.

COEFFICIENT OF THERMAL EXPANSION.

Finally, we often use the coefficient of thermal expansion

$$\alpha(T, p, X) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,X} \tag{2.38}$$

Again, we divide by the volume to scale out the system size. We also expect α to be positive. This is, however, not always true. There are materials with a negative coefficient of thermal expansion. These materials are exceptions, however.

RESPONSE FUNCTIONS FOR IDEAL GAS.

It is useful to calculate the values of the response functions for a mono-atomic ideal gas. This gives us a standard, a reference for comparison if we consider other systems. Using $U = \frac{3}{2}pV$ and $pV = NRT$ we find

$$C_V = \frac{3}{2}NR \tag{2.39}$$

$$C_p = \frac{5}{2}NR \tag{2.40}$$

$$\kappa_T = \frac{1}{p} \tag{2.41}$$

$$\kappa_S = \frac{3}{5p} \tag{2.42}$$

$$\alpha = \frac{1}{T} \tag{2.43}$$

The formula for κ_S follows from the formula for the entropy of an ideal gas 1.54, which implies that at constant entropy $V \propto T^{-\frac{3}{2}}$. Together with the ideal gas law this gives $V \propto p^{-\frac{3}{5}}$. The ideal gas values indeed satisfy $\kappa_T > \kappa_S > 0$ and $C_p > C_V > 0$.

Compressibilities are often given in a different form, by stating the relation between pressure and volume in the form $pV^\gamma = c$, where c is a constant and the value of γ depends on the process we consider. In an isothermal process at constant N we see from $pV = NRT$ that $\gamma = 1$, and in an adiabatic process at constant N we have $\gamma = \frac{5}{3}$.

There are some obvious problems with these numbers. We have seen before that at low temperature the heat capacities should approach zero, clearly not the case for the ideal gas. Also, at low temperature the expansion coefficient becomes infinite. This is due to the fact that the volume approaches zero. Also, the compressibilities diverge at zero pressure. All these facts point at the limitations of the model of an ideal gas. At low temperature this model is not valid.

Why is the ideal gas not a good model at low temperature?

2.6   Relations between partial derivatives.

Two derivatives.

Thermodynamics makes extensive use of the theory of calculus of many variables. This is a very powerful mathematical theory! It limits the changes in dependent variables. For example, response functions are partial derivatives, and they are related via Maxwell relations if they are also the second order derivatives of a free energy. Mathematics proves other relations between partial derivatives too. For example, assume we have a state function $z(x, y)$. It is possible to define a function $f(x, y, z)$ in such a way that $f(x, y, z) = 0$ leads exactly to this function. Hence $f(x, y, z(x, y)) \equiv 0$ for all values of x and y. The partial derivative of this identity with respect to x is

$$0 = \left(\frac{\partial f}{\partial x}\right)_{y,z} (x, y, z(x, y)) + \left(\frac{\partial f}{\partial z}\right)_{x,y} (x, y, z(x, y)) \left(\frac{\partial z}{\partial x}\right)_{y} (x, y) \qquad (2.44)$$

In a similar way, we can use $f(x, y, z) = 0$ to define a function $x(y, z)$, with $f(x(y, z), y, z) \equiv 0$. The partial derivative of this equation with respect to z is:

$$0 = \left(\frac{\partial f}{\partial x}\right)_{y,z} (x(y, z), y, z) \left(\frac{\partial x}{\partial z}\right)_{y} (y, z) + \left(\frac{\partial f}{\partial z}\right)_{x,y} (x(y, z), y, z) \qquad (2.45)$$

Comparing these two relations shows that for any point (x_0, y_0, z_0) obeying $f(x_0, y_0, z_0) = 0$ we have

$$\left(\frac{\partial z}{\partial x}\right)_{y} (x_0, y_0) \left(\frac{\partial x}{\partial z}\right)_{y} (y_0, z_0) = 1 \qquad (2.46)$$

when the partial derivatives of $f(x, y, z)$ are zero in isolated points only, and the partial derivatives of x and z are continuous. Hence given a state function $z(x, y)$ we can use z as a state variable and change variables to $\{y, z\}$, which defines a new state function $x(y, z)$. Partial derivatives of these two functions are related.

THREE DERIVATIVES.

A more surprising result is obtained when all three combinations of independent variables are used. Using $\{x, y\}$ as independent variables we have as before

$$-\left(\frac{\partial f}{\partial x}\right)_{y,z} (x, y, z(x, y)) = \left(\frac{\partial f}{\partial z}\right)_{x,y} (x, y, z(x, y)) \left(\frac{\partial z}{\partial x}\right)_{y} (x, y) \qquad (2.47)$$

In a similar way we obtain

$$-\left(\frac{\partial f}{\partial y}\right)_{x,z} (x(y, z), y, z) = \left(\frac{\partial f}{\partial x}\right)_{y,z} (x(y, z), y, z) \left(\frac{\partial x}{\partial y}\right)_{z} (y, z) \qquad (2.48)$$

$$-\left(\frac{\partial f}{\partial z}\right)_{x,y} (x, y(x, z), z) = \left(\frac{\partial f}{\partial y}\right)_{x,z} (x, y(x, z), z) \left(\frac{\partial y}{\partial z}\right)_{x} (x, z) \qquad (2.49)$$

Multiplying these equations leads to

$$\left(\frac{\partial x}{\partial y}\right)_{z} (y_0, z_0) \left(\frac{\partial y}{\partial z}\right)_{x} (x_0, z_0) \left(\frac{\partial z}{\partial x}\right)_{y} (x_0, y_0) = -1 \qquad (2.50)$$

for all points (x_0, y_0, z_0) obeying $f(x_0, y_0, z_0) = 0$, with similar assumptions one the partial derivatives as before. This relation is surprising because of the minus sign. It is often found in the form

$$\left(\frac{\partial x}{\partial y}\right)_z (y_0, z_0) = -\left(\frac{\partial x}{\partial z}\right)_y (y_0, z_0) \left(\frac{\partial z}{\partial y}\right)_x (x_0, y_0) \qquad (2.51)$$

This rule can be generalized to arbitrary numbers of variables. It is not hard to show that a minus sign always occurs when the total number of variables is odd.

DIFFERENCE OF HEAT CAPACITIES.

As an example, consider the state variables temperature T, pressure p, volume V, and the extensive variable(s) X. Considering the entropy as a function of $\{T, V, X\}$ gives $S_1(T, V, X)$ and considering the entropy as a function of $\{T, p, X\}$ gives a different function $S_2(T, p, X)$. These two functions are clearly related by

$$S_2(T, p, X) = S_1(T, V(T, p, X), X) \qquad (2.52)$$

where V(T,p,X) is the function for the equilibrium volume with $\{T, p, X\}$ as independent variables. Remember that *all these relations only hold for equilibrium systems*! Therefore the partial derivatives are related by

$$\left(\frac{\partial S_2}{\partial T}\right)_{p,X} = \left(\frac{\partial S_1}{\partial T}\right)_{V,X} + \left(\frac{\partial S_1}{\partial V}\right)_{T,X} \left(\frac{\partial V}{\partial T}\right)_{p,X} \qquad (2.53)$$

Using the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_{T,X} = -\left(\frac{\partial^2 F}{\partial V \partial T}\right)_X = \left(\frac{\partial p}{\partial T}\right)_{V,X} \qquad (2.54)$$

and the chain rule

$$\left(\frac{\partial p}{\partial T}\right)_{V,X} = -\left(\frac{\partial p}{\partial V}\right)_{T,X} \left(\frac{\partial V}{\partial T}\right)_{p,X} \qquad (2.55)$$

we then derive

$$C_p - C_V = \frac{VT\alpha^2}{\kappa_T} \qquad (2.56)$$

which tells us that $C_p > C_V$ indeed if $\kappa_T > 0$.

IMPORTANT POINTS.

In this derivation we did two things. First, we write these equations in terms of functions, leaving out the variables, since they are all contained in

the partial derivatives. For example, $\left(\frac{\partial S}{\partial V}\right)_{T,X}$ clearly is related to $S_1(T, V, X)$, while $\left(\frac{\partial S}{\partial p}\right)_{T,X}$ would imply $S_2(T, p, X)$. Even though in the partial derivatives we write the same symbol S in the top part, which is correct since in both cases the result of the function is the entropy, the functional form is understood to be different since the variables are different. This is probably the most confusing aspect of the notation used in calculus of many variables. Second, there are several ways to get from the beginning to the end. We started by using 2.54 since often it is a good idea to get rid of the entropy. In order to do that we either use the definition of heat capacity, or a Maxwell relation.

RATIOS OF RESPONSE FUNCTIONS.

In a similar way we find

$$\kappa_T - \kappa_S = \frac{VT\alpha^2}{C_p} \tag{2.57}$$

and from the ratio of these expressions we find

$$\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S} \tag{2.58}$$

which is a remarkably simple relation between very different response functions. Note that the last three formulas hold *for all systems, temperatures, pressures, etc.* Of course, on has to measure C_p and C_V at the same temperature and pressure in order to be able to compare them. These relations are experimentally confirmed. The most important message here is that many response functions are dependent and such dependencies give a good consistency check for experimental results. The ideal gas values do obey these relations, as can be easily checked. The fact that such relations exist is based on the fact that the function $U(S, V, N, X)$ gives a complete description of the system and that all other state variables follow from this function.

Check that 2.58 holds for the ideal gas.

Equation 2.58 has an interesting consequence. Suppose we have an ideal gas, but this gas is not mono-atomic. In that case we still have $pV = NRT$, but the energy versus temperature relation is more complicated. The isothermal compressibility κ_T ia still equal to $\frac{1}{p}$, which means that the adiabatic compressibility is given by:

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,N} = \kappa_S = \frac{1}{p}\frac{C_V}{C_p} \tag{2.59}$$

or

$$\left(\frac{\partial V}{\partial p}\right)_{S,N} = -\frac{V}{p}\frac{C_V}{C_p} \tag{2.60}$$

Suppose that we have a range of volumes for which the temperature changes while compressing are such that the ratio $\frac{C_V}{C_p}$ remains constant. Such a range is often found for polyatomic gases. For example, at some intermediate temperatures all rotational degrees of freedom might be active, but the vibrational are not. In that case we find for adiabatic compression that $p \propto V^{-\gamma}$ with $\gamma = \frac{C_p}{C_V}$. The coefficient of thermal expansion for this poly-atomic gas is still determined by $pV = NRT$, and hence $\alpha = \frac{1}{T}$. Equation 2.56 then tells us that $C_p - C_V = NR$, and hence $\gamma = 1 + \frac{NR}{C_V}$. Therefore, measuring the compressibility gives us the heat capacity, from which we can derive information about the internal degrees of freedom of the molecules!

2.7   Conditions for equilibrium.

PATH TO EQUILIBRIUM.

What happens when two equilibrium systems are brought into contact? Obviously, the combined system will try to reach thermal equilibrium. What are the conditions for this total equilibrium? These conditions are easy to derive if the combined system is completely isolated or closed, and cannot exchange energy in the form of work with the rest of the world. Heat exchange is possible, though. This means that the total volume, amount of material, etc. is constant. We also assume that we can keep the entropy of the system constant. This does not conflict with the statement that heat transfer is possible, since we consider non-equilibrium systems!

The two subsystems are able to exchange energy by changing their individual volumes ($\Rightarrow$ *mechanical* work), amount of material ($\Rightarrow$ *chemical* work), or entropies ($\Rightarrow$ *heat* exchange). We will label the two subsystems l for left and r for right. The total internal energy is

$$U_t = U_r + U_l \tag{2.61}$$

with

$$U_t = U(S, V, N, X) \tag{2.62}$$

$$U_l = U(S_l, V_l, N_l, X_l) \tag{2.63}$$

$$U_r = U(S - S_l, V - V_l, N - N_l, X - X_l) \tag{2.64}$$

where we use the symbol U for the function that gives the values U_l, U_r, U_t for the (sub)systems, and where X stands for all other extensive variables. Since the total system is closed, the total internal energy in equilibrium will be a minimum. Also the total sum of each extensive variable cannot change, and we have $S = S_l + S_r$, etc. The equilibrium state follows by minimizing the internal energy as a function of the four internal (for the total system) variables $\{S_l, V_l, N_l, X_l\}$. This leads to four equations of the form

$$\left(\frac{\partial U}{\partial S}\right)_{V,N,X} (S_l, V_l, N_l, X_l) - \left(\frac{\partial U}{\partial S}\right)_{V,N,X} (S - S_l, V - V_l, N - N_l, X - X_l) = 0$$

(2.65)

Using the expression for the differential dU we then see immediately that the conditions for equilibrium are:

$$T_l = T_r, p_l = p_r, \mu_l = \mu_r, x_l = x_r \tag{2.66}$$

All intensive variables have to be the same. This is of course exactly what we expected.

Using the minimum principle.

At this point we only used the fact that the internal energy is an extremum at equilibrium. We also know that is should be a minimum, and this gives a number of very useful inequalities for the second order derivatives. Assume that both subsystems are identical. Assume that the total entropy is 2S, the total volume 2V, etc. Using identical systems is just for convenience, but does not affect the general conclusion. The entropy of the system on the left is $S + \Delta S$ and for the system on the right $S - \Delta S$. The volume and all other extensive quantities are defined in a similar way. The difference in internal energy of the total system between equilibrium ($\Delta S = 0$, etc) and non-equilibrium is:

$$\Delta U = U(S + \Delta S, V + \Delta V, N + \Delta N, X + \Delta X) +$$
$$U(S - \Delta S, V - \Delta V, N - \Delta N, X - \Delta X) - 2U(S, V, N, X) \tag{2.67}$$

The changes ΔS, ΔV, ΔN, and ΔX in this formula are independent and can be chosen arbitrarily. The total energy is a minimum as a function of the internal variables $\{\Delta S, \Delta V, \Delta N, \Delta X\}$, and hence $\Delta U \geq 0$. Since the values of $\{S, V, N, X\}$ are arbitrary, this means that $U(S, V, N, X)$ is a <u>convex function</u>.

Consequences for second order derivatives.

The previous discussion was true for any value of the parameters ΔS, etc. When these changes are small, however, we can use a Taylor series expansion for the energy of the subsystems. The zeroth order term vanishes by construction. The first order term gives us the equilibrium conditions for the intensive state

variables we derived before. Hence we can write T for the temperature of the whole system and do not have to specify left or right. The same holds for all other intensive variables. The second order terms form an expression of the form

$$\Delta U = \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N,X} (\Delta S)^2 + \left(\frac{\partial^2 U}{\partial S \partial V}\right)_{N,X} \Delta S \Delta V + \cdots \qquad (2.68)$$

This expression has to be convex. By changing only one extensive variable at the time we find the necessary inequalities on the state function $U(S, V, N, X)$ of a *single* system:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N,X} \geq 0 \qquad (2.69)$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N,X} \geq 0 \qquad (2.70)$$

$$\left(\frac{\partial^2 U}{\partial N^2}\right)_{S,V,X} \geq 0 \qquad (2.71)$$

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_{S,V,N} \geq 0 \qquad (2.72)$$

This is not all, however. Suppose we only change S and V, in which case we have

$$\Delta U = \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N,X} (\Delta S)^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right)_{N,X} \Delta S \Delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N,X} (\Delta V)^2 \geq 0 \qquad (2.73)$$

If we divide by $(\Delta V)^2$ we have an inequality of the form $ax^2 + bx + c \geq 0$, which has to hold for all values of x. We already determined that $a \geq 0$ and $c \geq 0$. The form $ax^2 + bx + c$ has two distinct roots when $b^2 > 4ac$. In our case we therefore need $b^2 \leq 4ac$, or

$$\left(\left(\frac{\partial^2 U}{\partial S \partial V}\right)_{N,X}\right)^2 \leq \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N,X} \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N,X} \qquad (2.74)$$

HEAT CAPACITIES ARE POSITIVE.

These inequalities have a number of consequences for the signs of response functions. For example, $\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N,X} = \left(\frac{\partial T}{\partial S}\right)_{V,N,X} = \frac{T}{C_V}$. Since the temperature is positive (the existence of negative temperature values violates the second law), we find

$$C_V \geq 0 \tag{2.75}$$

or the specific heat at constant volume must be positive. This can be related to a condition for local stability. Consider a small volume in a large system in equilibrium. Due to some fluctuation the energy inside this volume is larger than average. If we would have $C_V < 0$, the temperature of this volume would be *less than average*! Due to the second law, energy would flow into this volume, making this fluctuation in energy even larger. Therefore a system with $C_V < 0$ is unstable against fluctuations in the energy. Stability therefore requires positive heat capacities at constant volume.

COMPRESSIBILITIES ARE POSITIVE.

Similarly, we find from the condition for $\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N,X}$ that

$$\kappa_S \geq 0 \tag{2.76}$$

Compressibilities also have to be positive because of a local stability argument. Suppose a small volume element has a pressure less than average. The outside environment has a larger pressure and hence will the imbalance of forces will reduce the volume of the small element. If the compressibility would be negative, the inside pressure would reduce even more and the process would run away. Therefore, a negative compressibility implies an instability against small fluctuations in the pressure.

THE MORE MATERIAL WE HAVE, THE HARDER IS IT TO ADD SOME.

The stability requirement for the chemical potential is

$$\left(\frac{\partial \mu}{\partial N}\right)_{S,V} \geq 0 \tag{2.77}$$

which implies that the energy μ it takes to add one unit mass of material to a system increases when the amount of material increases. It is harder to add material to a system which already contains a lot! This is again connected with a local stability requirement for fluctuations in the number of particles.

Finally we can use equation 2.74 to get

$$\frac{T}{V\kappa_S C_V} \geq \left(\left(\frac{\partial^2 U}{\partial S \partial V}\right)_{N,X}\right)^2 = \left(\left(\frac{\partial T}{\partial V}\right)_{S,N,X}\right)^2 \tag{2.78}$$

The chain rule gives

$$\left(\frac{\partial T}{\partial V}\right)_{S,N,X} = -\left(\frac{\partial T}{\partial S}\right)_{V,N,X}\left(\frac{\partial S}{\partial V}\right)_{T,N,X} \tag{2.79}$$

The first factor on the right hand side is $\frac{T}{C_V}$, while the second is transformed according to the Maxwell equation

$$\left(\frac{\partial S}{\partial V}\right)_{T,N,X} = \left(\frac{\partial p}{\partial T}\right)_{V,N,X} \tag{2.80}$$

Another application of the chain rule gives

$$\left(\frac{\partial p}{\partial T}\right)_{V,N,X} = -\left(\frac{\partial p}{\partial V}\right)_{T,N,X}\left(\frac{\partial V}{\partial T}\right)_{p,N,X} \tag{2.81}$$

or

$$\left(\frac{\partial p}{\partial T}\right)_{V,N,X} = -\frac{-1}{V\kappa_T}\alpha V \tag{2.82}$$

Combining everything gives

$$\frac{T}{V\kappa_S C_V} \geq \left(\frac{\alpha T}{C_V \kappa_T}\right)^2 \tag{2.83}$$

Multiplying these inequality by $\frac{C_V^2 V}{T}$, which is positive, and using 2.56 leads to

$$\frac{C_V}{\kappa_S} \geq \frac{C_p - C_V}{\kappa_T} \tag{2.84}$$

With the help of 2.75 and 2.58 we then find

$$\kappa_T \geq 0 \tag{2.85}$$

and hence due to 2.56

$$C_p \geq C_V \geq 0 \tag{2.86}$$

and using 2.57

$$\kappa_T \geq \kappa_S \geq 0 \tag{2.87}$$

The inequalities for the heat capacities and compressibilities hold for all systems. They have been derived without any knowledge of the function U(S,V,N,X), apart from the requirements of continuity of the second order derivatives and the restrictions due to the laws of thermodynamics. These are remarkable consequences indeed, based on minimal input.

Would it have been possible to derive these inequalities using the maximum entropy principle?

ON PARADOXES.

Consider a system where a thermally insulated piston can move back and forth in a closed cylinder. We have identical amounts of material in both parts of the cylinder, but they start out at different temperatures. At the start, both parts of the system are in thermal equilibrium, but they are not in equilibrium with each other. What do you expect that the equilibrium state is? The common answer is in the middle, with the temperatures and pressures on both sides equal to each other. Well, people have even done simulations showing that this is the case, so it must be true! But if you read the system description very carefully you will see that this is not true. Both parts of the system are thermally isolated. Assume that we take a path from the initial state to the final state along which each part of the system is always in equilibrium. The initial values of the entropy of the left and right sides are S_l and S_r, and these could be different. Equilibrium is obtained when

$$p_l = -\left(\frac{\partial U}{\partial V}\right)_{S,N} (V_l, S_l, N) = p_r = -\left(\frac{\partial U}{\partial V}\right)_{S,N} (V_r, S_r, N) \qquad (2.88)$$

with $V = V_l + V_r$. Only when $S_l = S_r$ does this lead to a stable situation with the piston in the middle.

A paradox is a result which *seems* to contradict common experience. They often arise from either not giving all information (like in our example), or by making a mistake in the analysis. Careful analysis will always show where we went wrong. For example, in the Gibbs paradox we obtain wrong results if we omit the N dependence of the constant of integration. Unfortunately, in thermodynamics we always deal with many variables, and the opportunity to create paradoxes is large. But as long as we always first determine the set of independent state variables for a given problem, we will avoid many of these paradoxes.

2.8   Stability requirements on other fee energies.

The conditions for equilibrium discussed in the previous section can be generalized to all thermodynamic potentials as a function of *extensive* variables. It does not hold for intensive variables, though. As an example, consider the Gibbs free energy G(T,p,N). It is easy to show that

$$\left(\frac{\partial^2 G}{\partial N^2}\right)_{p,T} \geq 0 \qquad (2.89)$$

using the same thought experiment as before. But these experiments do not work for intensive variables. It is not possible, for example, to exchange an amount of temperature. On the other hand, one can calculate the second order derivatives in this case directly:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} = -\left(\frac{\partial S}{\partial T}\right)_{p,N} = -\frac{C_p}{T} \leq 0 \qquad (2.90)$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N} = \left(\frac{\partial V}{\partial p}\right)_{T,N} = -V\kappa_T \leq 0 \qquad (2.91)$$

and the signs are opposite from what we find for the extensive variables. On the other hand

$$\left(\frac{\partial^2 G}{\partial p \partial T}\right)_{N} = \left(\frac{\partial V}{\partial T}\right)_{p,N} = \alpha V \qquad (2.92)$$

and this leads to

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N}\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N} - \left(\left(\frac{\partial^2 G}{\partial p \partial T}\right)_{N}\right)^2 =$$

$$\frac{V\kappa_T C_p}{T} - \alpha^2 V^2 = \frac{V\kappa_T C_V}{T} \geq 0 \qquad (2.93)$$

where we used 2.56. As a result we find that G(p,T,N) is **concave** as a function of **p and T**, but **convex** as a function of **N**. Note that these conclusions are independent of the minimum property of the Gibbs free energy. In that case we have the statement that at given values of p,T, and N the Gibbs free energy in equilibrium is a minimum as a function of the *internal* degrees of freedom!

ENTROPY RELATIONS.

We can also perform the thought experiment for a completely closed system, in which no heat is allowed to go to the external world. In that case we specify U,V,N,X for the total system. The equilibrium state is found by maximizing the entropy. Because the nature of the extremum has now changed to a maximum, this implies that S(U,V,N,X) is a concave function. As a consequence we have

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N,X} \leq 0 \qquad (2.94)$$

$$\left(\frac{\partial^2}{\partial V^2}\right)_{U,N,X} \leq 0 \qquad (2.95)$$

$$\left(\frac{\partial^2 S}{\partial N^2}\right)_{V,U,X} \leq 0 \qquad (2.96)$$

$$\left(\frac{\partial^2 S}{\partial X^2}\right)_{U,V,N} \leq 0 \qquad (2.97)$$

with opposite signs from what we found for the second order derivatives of the internal energy. But we still have the additional requirements of the form

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N,X} \left(\frac{\partial^2 S}{\partial V^2}\right)_{U,N,X} \geq \left(\left(\frac{\partial^2 S}{\partial U \partial V}\right)_{N,X}\right)^2 \tag{2.98}$$

as before. Here the sign does not change because these requirements are related to a no-root condition.

It is interesting to compare the derivatives containing S and U. We derived in general that

$$\left(\frac{\partial S}{\partial U}\right)_{V,N,X} \left(\frac{\partial U}{\partial S}\right)_{V,N,X} = 1 \tag{2.99}$$

Such a simple relation does not hold for the second order derivatives. From the inequalities we find

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N,X} \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N,X} \leq 0 \tag{2.100}$$

2.9 A magnetic puzzle.

WHAT IS WRONG?

Consider a magnetic system, in which the basic extensive variables are the entropy S, volume V, amount of material N, and total magnetic moment M. The magnetic work term is given by

$$\bar{d}W_{mag} = -HdM \tag{2.101}$$

where we assume that the direction of the applied field and the direction of the resulting moment are always the same. We define the magnetic susceptibilities by

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T \tag{2.102}$$

and

$$\chi_S = \left(\frac{\partial M}{\partial H}\right)_S \tag{2.103}$$

In problem 7 we analyze this, and we find that the normal stability requirements demand that

$$\chi_T \geq \chi_S \geq 0 \tag{2.104}$$

for all materials, all values of the temperature, pressure, etc.

This is very similar to the case of compressibilities, and in experiments compressibilities are always positive. What could go wrong here? Well, there are many *diamagnetic* materials, for which the susceptibilities are negative!

POSSIBLE SOLUTIONS.

One possible answer is that thermodynamics is wrong. Before we take this drastic step, however, it is advisable to consider other possibilities. Could the experiments be wrong? No, they are not. Is there some physics missing? Is there anything that takes up energy? Yes! In order to apply a field we create a field in the material, and this magnetic field also needs energy! Therefore, the work term is incomplete. We need to include an extra term that accounts for the energy stored in the field.

SOME BASIC E&M.

Suppose we have the situation in which the magnetic field $\vec{H}(\vec{r}, t)$ changes from zero at t=0 to some value. Assume that this change is infinitesimally slow, and that the partial derivatives with time are very small. How much energy is stored in the field? An applied field is caused by some current density $\vec{j}(\vec{r}, t)$ and we assume that this current density slowly changes from zero to its final value. In that case we have at all times:

$$\vec{\nabla} \times \vec{H} = \vec{j} \tag{2.105}$$

in appropriate units (MKSA).

In order to create the current density $\vec{j}$ we need some EMF. However, when we change the current density we change the magnetic field and hence we create an electric field according to

$$\vec{\nabla} \times \vec{E} = -\left(\frac{\partial \vec{B}}{\partial t}\right) \tag{2.106}$$

and this E-field will act on the current density and work will be done. The amount of work done in a small time dt is

$$\bar{d}W = dt \int_{space} d^3r \vec{E} \cdot \vec{j} \tag{2.107}$$

Next we have to make sure that we understand the sign in this equation. The charges represented in the current loose potential energy when they follow the E-field, and hence this term represent a loss of potential energy of the current density (the source of outside energy) and this energy is returned to the EMF

driving the current density. Hence the work above is work done on the outside, or on the source of the magnetic field.

The work equation is easily transformed into a more standard form. Using 2.105 we find

$$\bar{d}W = dt \int_{space} d^3r \vec{E} \cdot \vec{\nabla} \times \vec{H} \tag{2.108}$$

and using

$$\vec{\nabla} \cdot (\vec{A} \times \vec{B}) = \vec{B} \cdot (\vec{\nabla} \times \vec{A}) - \vec{A} \cdot (\vec{\nabla} \times \vec{B}) \tag{2.109}$$

we get

$$\bar{d}W = -dt \int_{space} d^3r \left[\vec{\nabla} \cdot (\vec{E} \times \vec{H}) - \vec{H} \cdot \vec{\nabla} \times \vec{E} \right] \tag{2.110}$$

The first term can be transformed to a surface integral and since we integrate over all space this integral vanishes. The second term is transformed with 2.106 to:

$$\bar{d}W = -dt \int_{space} d^3r \vec{H} \cdot \left(\frac{\partial \vec{B}}{\partial t} \right) = - \int_{space} d^3r \vec{H} \cdot d\vec{B} \tag{2.111}$$

Magnetic work complete.

Next we separate space into two parts. Everything outside the volume V of our material is treated as part of the outside world, and changes in field energy in the outside world are simple part of the machinery that generates the magnetic field in the first place. Hence they are of no concern. We only consider the work term that stores energy in the field in our sample.

Next, we assume that all fields inside the sample are homogeneous. Also, we assume that the H and B field have the same direction. These conditions are not essential, but simply make the formulas somewhat easier. It is not hard to write down the general case. We find:

$$\bar{d}W_{mag} = -VHdB \tag{2.112}$$

The B field and the H field are related via the magnetic moment density according to

$$\vec{B} = \mu_0 (\vec{H} + \frac{1}{V}\vec{M}) \tag{2.113}$$

and therefore the magnetic work is

$$\bar{d}W_{mag} = -\mu_0 VHdH - \mu_0 HdM \tag{2.114}$$

which is the work done on the outside world by the sample. The second term is as expected, increasing the magnetic moment requires energy. The first term means that increasing the field *in the region of the sample* also requires energy, and that this energy is proportional to H^2.

UNITS ARE NOT ALWAYS OBVIOUS IN E&M.

In thermodynamics we are used to seeing the formulas for magnetic work without the constants μ_0. This is not hard to accomplish, as long as we remember to use the correct units. To obtain Gaussian units we make the following replacements:

$$H \rightarrow \frac{1}{\sqrt{4\pi\mu_0}}H \tag{2.115}$$

$$M \rightarrow \frac{\sqrt{4\pi}}{\sqrt{\mu_0}}M \tag{2.116}$$

and in Gaussian units we have

$$\bar{d}W_{mag} = -\frac{V}{4\pi}HdH - HdM \tag{2.117}$$

INTERPRETATION.

The work term in 2.117 includes a term that does not depend on the magnetization of the material. If we do an experiment to measure the magnetic susceptibility and leave out the sample, we would still measure an effect, since we are storing energy in the magnetic field in the region where the sample would have been. The first term in 2.117 is really not a term connected with a sample, and should be subtracted. This is, however, never done in practice, and *one always measure the total response of sample and field together*, and defines the susceptibility from that total response. If we would subtract the energy stored in the field, susceptibilities would be positive indeed.

EXPERIMENTALLY MEASURED SUSCEPTIBILITIES.

A simple relation between the B and H fields is given by $B = \mu H$, which combines with $H = B - \frac{4\pi}{V}M$ (Gaussian units!) gives

$$(\mu - 1)H = \frac{4\pi}{V}M \tag{2.118}$$

from which we derive

$$\bar{d}W = -\frac{\mu}{\mu - 1}HdM \tag{2.119}$$

or by defining $M' = \frac{\mu}{\mu-1}M$ we have in this new variable

$$\bar{d}W = -HdM' \tag{2.120}$$

exactly as we had before we introduced the energy in the field. In terms of this new variable M' we have therefore:

$$\left(\frac{\partial^2 U}{\partial M'^2}\right) \geq 0 \tag{2.121}$$

or

$$\left(\frac{\partial H}{\partial M'}\right) \geq 0 \tag{2.122}$$

or

$$\frac{\mu - 1}{\mu}\frac{1}{\chi} \geq 0 \tag{2.123}$$

But we also have using 2.118

$$\chi = \left(\frac{\partial M}{\partial H}\right) = V\frac{\mu - 1}{4\pi} \tag{2.124}$$

which leads to

$$\frac{4\pi}{\mu V} \geq 0 \tag{2.125}$$

or

$$\mu \geq 0 \tag{2.126}$$

In other words, the permeability is a positive quantity. The consequence for the susceptibility is then from 2.124 that

$$\chi \geq -\frac{V}{4\pi} \tag{2.127}$$

which is indeed observed experimentally.

2.10 Role of fluctuations.

In this section we take a first look at the role of fluctuations in materials. A natural explanation of phenomena related to fluctuations is given in statistical mechanics, where we consider the atomic nature of materials on a microscopic scale. In this section we look at fluctuations on a larger scale, and derive some conclusions which should always be valid, independent of the atomic nature of the material. This again gives us some basic relations which a true microscopic theory should obey. This is another example of the limits set by thermodynamics on microscopic theories.

A SMALL SUBSYSTEM.

Consider a system with volume V_L, amount of material N_L, and energy U_L. These quantities are fixed and completely define the system. In other words, the temperature T_L, the pressure p_L, and the chemical potential μ_L of the system are completely defined in equilibrium. Also, the entropy S_L of the system in equilibrium is determined.

Consider a small part of this system. In order to define a small part, we need at least on extensive variable. The natural variable is to use the volume, although one could also use the amount of material. Hence we consider a small volume V inside the system. We know that on average we have for the energy U and the amount of material N in this subsystem:

$$U = U_L \frac{V}{V_L} \tag{2.128}$$

and

$$N = N_L \frac{V}{V_L} \tag{2.129}$$

The energy and the amount of material in the subsystem can fluctuate by amounts ΔU and ΔN, however, and as derived before we have for the entropy of the subsystem:

$$S(U + \Delta U, V, N + \Delta N) = S(U, V, N) + \frac{1}{T_L}\Delta U - \frac{\mu_L}{T_L}\Delta N +$$

$$\frac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N}(\Delta U)^2 + \left(\frac{\partial^2 S}{\partial U \partial N}\right)_V \Delta U \Delta N + \frac{1}{2}\left(\frac{\partial^2 S}{\partial N^2}\right)_{U,V}(\Delta N)^2 + \cdots \tag{2.130}$$

which is exactly the relation we used to determine the equilibrium conditions for a stable material.

The discussion we had before used fluctuations to derive criteria for stability, by requiring that the entropy in equilibrium is maximal. This discussion does not answer the question how likely these fluctuations are to happen. In other words, what is the probability $W(\Delta U, \Delta N)$ of such a fluctuation? Which terms in the entropy should play a role?

SUBTRACTING THE REFERENCE VALUES.

The first term in 2.130 simply sets the value of the entropy as expected from equilibrium, when the total system is completely homogeneous. This is just a reference value. The linear terms determine the conditions for equilibrium, and show that $T = T_L$ and $\mu = \mu_L$ are needed. In equilibrium both the temperature and the chemical potential are uniform. Therefore we consider the function:

$$R(U, V, N, \Delta U, \Delta N) = S(U + \Delta U, V, N + \Delta N) - S(U, V, N) -$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} \Delta U - \left(\frac{\partial S}{\partial N}\right)_{U,V} \Delta N \tag{2.131}$$

where by definition we do not subtract terms with fluctuations in the volume, since the volume is considered to be a constant. This function R contains all higher order terms in the fluctuations. Also, this function is negative, since in equilibrium the entropy is a maximum. Therefore we have that $e^R \leq 1$ and this could perhaps be used for a probability. Another reason is that the law of large numbers tells us that the probability as a function of the fluctuations should be a Gaussian distribution for small fluctuations, and e^R has that form.

TWO NEW VARIABLES.

In order to make the math easier, we introduce two new variables:

$$X_U = \frac{1}{T_L} \tag{2.132}$$

and

$$X_N = -\frac{\mu_L}{T_L} \tag{2.133}$$

If we assume that the material in the volume V is in equilibrium with the total sample, we can then rewrite the function R in the form:

$$R(U, V, N, \Delta U, \Delta N) = S(U + \Delta U, V, N + \Delta N) - S(U, V, N) - X_U \Delta U - X_N \Delta N \tag{2.134}$$

The entropy is the extensive state variable describing the internal structure of a material. It is therefore reasonable to use the entropy as the state function that governs the probability of the fluctuations. Using the fact that for small fluctuations in the thermodynamic limit (V large, but always small compared to the total volume V_L) the probabilities need to be Gaussian we define for the probability W of a fluctuation in U and V:

$$W(\Delta U, \Delta N) = Ae^{\omega R(U, V, N, \Delta U, \Delta N)} \tag{2.135}$$

This definition contains two parameters, but the value of A is easily fixed by normalization:

$$\int Ae^{\omega R(U, V, N, \Delta U, \Delta N)} d\Delta U d\Delta N = 1 \tag{2.136}$$

The remaining question is how to find the value of ω. This requires microscopic theory or experiment. It turns out that $\omega R = 1$, a result easily explained in

statistical mechanics. This observation also allows us to connect macroscopic experiments with microscopic theory, since we can measure probability distributions of macroscopic fluctuations!

In equation 2.135, what is really new and unexpected? The basic form can be derived from the law of large numbers, which states that in the thermodynamic limit the probability distribution has to be Gaussian. This requires that the leading term in the exponent should be of the form

$$-A\left(\Delta U\right)^2 - B\Delta U\Delta N - C\left(\Delta N\right)^2 \qquad (2.137)$$

and that $A > 0$, $C > 0$, and $B^2 \leq 4AC$. It does not require any further relation between the values of A, B, and C, though. It also does not say anything about the higher order terms. Equation 2.135 limits how these coefficients are related. This has consequences for experimental observations, and relation based on 2.135 have been confirmed both theoretically (statistical mechanics) and experimentally.

AVERAGES.

The use of equation 2.135 follows from the calculation of average values. Suppose we have a state function f that depends on the amount of material and the energy in the volume V. We assume that the fluctuations are slow, and that the material in V is always in equilibrium internally (but not with the outside world, of course). We can then define an average of this function by

$$\langle f(\Delta U, \Delta N)\rangle = \int Ae^{\omega R(U,V,N,\Delta U,\Delta N)} f(\Delta U, \Delta N)d\Delta U d\Delta N \qquad (2.138)$$

Obviously we need to have $\langle \Delta U\rangle = 0$ and $\langle \Delta N\rangle = 0$.

Why is this obvious?

IGNORE HIGHER ORDER TERMS.

The definition 2.135 includes third order terms. Because of these terms, the probability distribution is not symmetric around the maximum value, and as a result a calculation of $\langle \Delta U\rangle$ using 2.135 might not produce zero. This seems to be a problem, until we realize that we have to take the thermodynamic limit (this thing is hidden everywhere!) and as a consequence the effects of the higher order terms become much smaller than those of the second order terms. Therefore we approximate the probability by

$$W(\Delta U, \Delta N) = Ae^{\omega\left(\frac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N}(\Delta U)^2 + \left(\frac{\partial^2 S}{\partial U \partial N}\right)_V \Delta U \Delta N + \frac{1}{2}\left(\frac{\partial^2 S}{\partial N^2}\right)_{U,V}(\Delta N)^2\right)}$$

(2.139)

Using this form in the thermodynamic limit will give the same results as using the original definition.

CONSEQUENCES.

As an example we study the case where only energy can fluctuate, and hence the amount of material in V is constant, or $\Delta N = 0$. Because $\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$ we have

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} = -\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_{V,N} = -\frac{1}{T^2 C_V}$$

(2.140)

and the probability for a fluctuation in the energy is

$$W(\Delta U) = Ae^{-\frac{\omega(\Delta U)^2}{2T^2 C_V}}$$

(2.141)

The calculation of the average mean square fluctuation is easy, and we find

$$\langle(\Delta U)^2\rangle = \frac{T^2}{\omega}C_V$$

(2.142)

This formula has some interesting consequences. Since the right hand side is extensive, the left hand side is proportional to N, and we have

$$\frac{\sqrt{\langle(\Delta U)^2\rangle}}{U} \propto \frac{1}{\sqrt{N}}$$

(2.143)

In other words, in the thermodynamic limit the relative magnitude of the fluctuations goes to zero!

A second interesting observation is that fluctuations are related to the corresponding response function. Materials with a large value of the heat capacity show large fluctuations in the energy. In other words, if we have a material with a large heat capacity a small fluctuation in the temperature will give a large fluctuation in the energy. Such materials apparently respond more dramatically to temperature fluctuations.

Both previous observations hold in general, and are useful to remember.

FLUCTUATIONS ARE CORRELATED.

What is the value of $\langle \Delta U \Delta N \rangle$? Naively one might say zero, but that is not true since we assume that the material in V is always in equilibrium. A change in U will change the chemical potential, and the effect of changes in N are now

dependent on how U is changing. This is related to the presence of the mixed term in the exponent in the definition of the probability. The form is

$$\left(\frac{\partial^2 S}{\partial U \partial N}\right)_V = -\frac{1}{T^2}\left(\frac{\partial T}{\partial N}\right)_{U,V} \tag{2.144}$$

which indeed relates changed in N to changes in T and hence changes in U.

A CALCULATIONAL TRICK.

We use 2.135 in connection with 2.134, and consider X_U and X_N to be independent variables, which in equilibrium will take the appropriate values related to the big system. This leads to

$$\left(\frac{\partial W}{\partial X_U}\right) = -\omega \Delta U W \tag{2.145}$$

and

$$\left(\frac{\partial W}{\partial X_N}\right) = -\omega \Delta N W \tag{2.146}$$

This leads to

$$\langle \Delta U \Delta N \rangle = -\frac{1}{\omega}\langle \Delta U \left(\frac{\partial W}{\partial X_N}\right)\frac{1}{W}\rangle \tag{2.147}$$

Using the definition of an average we find

$$\langle \Delta U \Delta N \rangle = -\frac{1}{\omega}\int \Delta U \left(\frac{\partial W}{\partial X_N}\right) d\Delta U d\Delta N \tag{2.148}$$

and using integration by parts

$$\langle \Delta U \Delta N \rangle = -\frac{1}{\omega}\frac{\partial}{\partial X_N}\int \Delta U W d\Delta U d\Delta N + \frac{1}{\omega}\int \left(\frac{\partial \Delta U}{\partial X_N}\right) W d\Delta U d\Delta N \tag{2.149}$$

The first term is zero because $\int \Delta U W d\Delta U d\Delta N = 0$. The second term contains

$$\left(\frac{\partial \Delta U}{\partial X_N}\right) = \left(\frac{\partial U_{instantaneous} - U}{\partial X_N}\right) = -\left(\frac{\partial U}{\partial X_N}\right) \tag{2.150}$$

since the instantaneous energy is an independent variable. This expression is also independent of the fluctuation, and we obtain

$$\langle \Delta U \Delta N \rangle = -\frac{1}{\omega}\left(\frac{\partial U}{\partial X_N}\right)_{V,X_U} \tag{2.151}$$

In a similar manner, eliminating ΔU, we could have obtained

$$\langle \Delta U \Delta N \rangle = -\frac{1}{\omega} \left(\frac{\partial N}{\partial X_U} \right)_{V,X_N} \tag{2.152}$$

which shows a type of relation between partial derivatives which is similar to the Maxwell relations discussed in this chapter.

We now use the last equation and use that X_U is in equilibrium determined by T_L via $X_U = \frac{1}{T_L}$ and obtain:

$$\langle \Delta U \Delta N \rangle = \frac{T^2}{\omega} \left(\frac{\partial N}{\partial T} \right)_{V,X_N} \tag{2.153}$$

where the partial derivative is calculated at equilibrium values corresponding to $V, T = T_L, \mu = \mu_L$. The only point of concern is that the partial derivative is calculated at constant X_N, or at constant $\frac{\mu}{T}$. Using that in this case $N(T,V,\mu) = N(T,V,X_N T)$ we derive

$$\left(\frac{\partial N}{\partial T} \right)_{V,X_N} = \left(\frac{\partial N}{\partial T} \right)_{V,\mu} + X_N \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \tag{2.154}$$

and we have for our final result

$$\langle \Delta U \Delta N \rangle = \frac{T}{\omega} \left[T \left(\frac{\partial N}{\partial T} \right)_{V,\mu} + \mu \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \right] \tag{2.155}$$

which indicates that the fluctuations in U and N are correlated, unless the partial derivatives cancel in a special way.

FLUCTUATIONS IN U AGAIN.

In a similar way we derive that

$$\langle (\Delta U)^2 \rangle = \frac{T^2}{\omega} \left(\frac{\partial U}{\partial T} \right)_{V,X_N} \tag{2.156}$$

and this differs from the form we derived before, because in the partial derivative X_N is held constant. This difference can be explained very easily. In the current calculation we allow both U and N to fluctuate, and we know that these are correlated. In the case we considered before we demanded that $\Delta N = 0$. The space over which the average value is calculated is therefore different, and the result will be different!

2.11 Extra equations.

1. *If the only state variables are T, S, p,and V,what is the meaning of $U - TS + pV$?*

2. *Why is there a difference in useful work done between a constant N and a constant /mu process?*

3. *Explain the three cylinder scenarios.*

4. *Give examples for the use of each free energy.*

5. *The natural variables for U are S, V, and N. Why does that make sense?*

6. *So we have $U = TS - pV + \mu N$ and also $U = TS - pV + \mu N + MH$. How can that be?*

7. *What is the importance of Euler and Gibbs-Duhem?*

8. *How many of the Maxwell relations should you memorize?*

9. *Should α always be positive?*

10. *For a negative thermal expansion material, would $C_p < C_V$?*

11. *Which additional response functions could one define in a magnetic system? How many heat capacities?*

12. *Which Maxwell to use?*

13. *What are the signs of an ideal gas model failing at low T?*

14. *Find a Maxwell relation to change $\left(\frac{\partial S}{\partial T}\right)_{V,N}$*

15. *Show that $\alpha = \frac{1}{V}\left(\frac{\partial^2 G}{\partial p \partial T}\right)_N = -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_N$*

16. *Minus sign in three derivative relation Why also in five, seven?*

17. *Why is the ratio relation for heat capacities, compressibilities important?*

18. *Explain why a negative compressibility leads to an instability*

19. *$f(x,y,z) = x^2 + y^2 + z^2 - R^2$. $x = \sqrt{R^2 - y^2 - z^2}$. $\left(\frac{\partial x}{\partial y}\right)_z = -\frac{y}{x}$ Is the chain rule OK?*

20. *Why is there a minimum only in the extensive variables?*

21. *Are there more relations to make sure that the entropy is a maximum?*

22. *What is the difference between H and T?*

23. *Which materials have $\chi = -\frac{V}{4\pi}$?*

24. *Is $\left(\frac{\partial \mu}{\partial N}\right)_{??}$ always positive, no mater which variables are held constant?*

25. *What kind of fluctuations can we describe?*

26. *Why use the entropy to characterize fluctuations?*

27. *Which R is in $\omega R = 1$?*

28. *Why do higher order terms drop out in the TD limit?*

29. *What are uses of the relation between $< (\Delta U)^2 >$ and C_V?*

30. *If the correlation between fluctuations cancel, what is the condition? ($\mu \propto T$!!)*

2.12   Problems for chapter 2

PROBLEM 1.

A container with volume V contains N moles of an ideal gas. The container is divided into two parts by a movable partition. This partition can move without any friction. The volume of the left part is V_1. The number of moles in the left part is N_1. The partition always moves infinitesimally slow, and the ideal gas in each part is always in equilibrium. The temperature is T everywhere in the system. T is kept constant. Material cannot go through the partition, hence N_1 remains constant. V_1 can vary, though, and hence we consider V_1 to be an internal parameter.

(a) Which thermodynamic potential does one have to minimize as a function of V_1 in order to find the equilibrium state of the total system?

(b) Show that the minimum occurs when the pressure left and right is the same. Note: do not only show that it is an extremum, but show that it is not a maximum!

PROBLEM 2.

Show that $\kappa_T - \kappa_S = \frac{V T \alpha^2}{C_p}$ (equation 2.57).

PROBLEM 3.

In first approximation, the electrons in a conductor can be modelled by a gas of particles at a given temperature T in a volume V at a chemical potential μ. The chemical potential is set by connecting the conductor to a battery, the other terminal of the battery is grounded.

(a) Which thermodynamic potential is needed to describe this system?

The number of electrons in the conductor is measured as a function of the temperature. Experimentally one finds the relation $N(T, V, \mu) = n_0 V (1 - \frac{RT}{\mu})$ for a range of temperatures with $RT \ll \mu$.

(b) Using a Maxwell relation, calculate how the entropy S depends on μ.

(c) Show that $\lim_{\mu \to 0} S(T, V, \mu) = \infty$.

The last result seems to indicate that $\lim_{T \to 0} S(T, V, 0) = \infty$, in contradiction with the third law.

(d) Argue that this experiment does not invalidate the third law.

PROBLEM 4.

Show that $\left(\frac{\partial \mu}{\partial N} \right)_{S,V} \leq \frac{C_V}{T} \left(\left(\frac{\partial T}{\partial N} \right)_{S,V} \right)^2$. Use this expression for $\mu(S, V, N)$ to show that $\left(\frac{\partial \mu}{\partial N} \right)_{T,V} \geq 0$.

PROBLEM 5.

Show that the energy function $U(S, V) = \frac{S^2}{V}$ satisfies the criteria for stability. Calculate C_V, C_p, κ_S, κ_T, and α for this system as a function of the temperature T.

PROBLEM 6.

Calculate $\left(\frac{\partial^2 S}{\partial U^2} \right)_{V,N,X}$ and $\left(\frac{\partial^2 U}{\partial S^2} \right)_{V,N,X}$ in terms of response functions discussed in this chapter. Use these results to show that the product of these two derivatives is negative.

PROBLEM 7.

A magnetic system is characterized by the state variables T, S, M, H, μ, and N. N is always constant in this problem. All partial derivatives are at constant N. The magnetic susceptibilities are defined by $\chi_T = \left(\frac{\partial M}{\partial H} \right)_T$ and $\chi_S = \left(\frac{\partial M}{\partial H} \right)_S$.

(a) Show that the heat capacities at constant field and at constant moment are related to the susceptibility χ_T by $C_H - C_M = \frac{T}{\chi_T} \left(\left(\frac{\partial M}{\partial T} \right)_H \right)^2$.

(b) Show that the susceptibilities at constant temperature and entropy obey $\chi_T - \chi_S = \frac{T}{C_H} \left(\left(\frac{\partial M}{\partial T} \right)_H \right)^2$.

(c) Show that $\chi_T \geq \chi_S \geq 0$ and that $C_H \geq C_M \geq 0$.

(d) Calculate C_H, C_M, χ_T, and χ_S for a paramagnetic gas containing N moles of material with $U = \frac{3}{2}NRT$ and $M = \frac{CNH}{T}$.

PROBLEM 8.

Show that $\langle (\Delta M)^2 \rangle = \frac{T}{\omega} \chi_V$ when $\Delta U = \Delta N = 0$.

PROBLEM 9.

A closed system (no exchange of heat and work with the outside world) contains an ideal gas. The volume V of the total system is constant. An internal partition divides the system in two parts. There is no flow of material through this partition. The volumes of the two parts are V_1 and $V - V_1$. The parameter V_1 is an internal parameter. Heat can flow back and forth through the partition. As a consequence, the temperature T is always the same left and right, and is equal to $T(V_1)$. The partition always moves in a quasi-static manner and each part of the system is always in thermal equilibrium. The internal energy of the system is the sum of the internal energy of the parts plus the mechanical potential energy of the partition (the pressures in both parts are not the same!). The total entropy of the system is constant.

(a) Use the entropy equation for an ideal gas to find $\left(\frac{\partial T}{\partial V_1} \right)$ as a function of V_1.

(b) Use this result to show that in equilibrium the temperature of a system with given S, V, and N is a minimum.

(c) The minimum energy principle in connection with $U = \frac{3}{2}NRT$ seems to lead to the same conclusion. What is wrong in that argument?

PROBLEM 10.

A gas has the equation of state $pV = NRT$, but does not have to be ideal, hence U does not have to be pV. The volume expands by a small amount ΔV at constant temperature and constant number of particles.

(A) Use a Maxwell relation to calculate $\left(\frac{\partial S}{\partial V} \right)_{TN}$.

(B) Calculate the amount of work ΔW done during this process, in terms of state variables and ΔV.

(C) Calculate the amount of heat ΔQ entering the system during this process, in terms of state variables and ΔV.

(D) Show that $\Delta U = 0$ during this process.

(E) If (D) is true, show that U is a function of T and N only.

(F) If (E) is true, show that U has the form $U = Nf(T)$.

PROBLEM 11.

Two containers are connected by a valve. The first container, volume V, contains a gas at temperature T, pressure p. The second container is empty (vacuum). The total volume of both containers is V'. Both containers are completely isolated from the environment. The valve is opened, and the gas in the first container expands freely, but irreversibly, and finally fills both containers. In the end we have again thermodynamic equilibrium, with state variables V', T', and p'. Calculate T' in the following two cases: (a) the gas is ideal (b) the gas has equations of state $(p + a\frac{N^2}{V^2})(V - Nb) = NRT$, $C_V = \frac{3}{2}NR$.

PROBLEM 12.

Show that the osmotic pressure p exerted by N moles of solute in a very dilute solution of temperature T and volume V is given by $p = \frac{NRT}{V}$. Use entropy arguments.

PROBLEM 13.

The function U is given by $U(S, V, N) = \frac{1}{N}(S^2 + S - V^2)$. Give three reasons why this is not a correct function describing the internal energy of a material.

PROBLEM 14.

The internal energy of system is given by $U(S, V, N) = S^\alpha V^\beta N^\gamma$.

(a) Using the fact that U is extensive, find a relation between α, β, and γ.

(b) Calculate the pressure p, temperature T, and chemical potential μ as a function of S, V, and N.

(c) Calculate the heat capacity at constant volume V (and constant N).

(d) Calculate the adiabatic compressibility (at constant N).

(e) Based on the sign of these response functions, find inequalities for α and β.

PROBLEM 15.

Use a Maxwell relation to relate the coefficient of thermal expansion to a
partial derivative of the entropy and use that to show that the coefficient of
thermal expansion approaches zero when the temperature goes to zero.

PROBLEM 16.

A system is characterized by four state variables, S, T, p, and V. The internal
energy is given by

$$U(T,V) = cVT^2$$

with c being a constant.

(A) Calculate $\left(\frac{\partial S}{\partial T}\right)_V$.

(B) Calculate $S(T,V)$.

(C) Calculate $p(T,V)$.

PROBLEM 17.

The equations of state for an ideal gas are $pV = NRT$ and $U = \frac{3}{2}NRT$.

(A) Show that $C_V = \frac{3}{2}NR$.

(B) Calculate the entropy difference $S(T,V,N) - S(T_0,V,N)$.

(C) What happens in the limit $T \to 0$? Which conclusion can you draw from
this?

(D) Calculate the enthalpy H.

(E) Use the enthalpy to show that $C_p = \frac{5}{2}NR$.

PROBLEM 18.

The chemical potential of an ideal gas with density $n = \frac{N}{V}$ is given by

$$\mu = RT \ln(\frac{n}{n_G})$$

with $n_G = cT^{\frac{3}{2}}$, where c is a constant with the appropriate dimensions. This
gas is put in a uniform gravitational filed, acceleration g. Calculate the pressure
in this isothermal gas as a function of height.

PROBLEM 19.

A steam engine works changing water to steam, and using the steam's pressure to do mechanical work. Consider a steam engine pulling a train of cars (no friction), holding water and fuel. At the beginning the mass of the empty train is M, the mass of the water is M_{water}, and the mass of the fuel is M_{fuel}. A unit mass of fuel releases J Joules upon burning. This energy evaporates the water and brings the steam to 200C. The heat per mole needed to do this is H. Mechanical energy is gained from the steam by adiabatically cooling it to 100C. The adiabatic index γ of water is $\frac{4}{3}$.

(a) Calculate the fraction f of the fuel's energy that is available to do mechanical work.

(b) The train moves up a hill on a 10km stretch with a 1% slope. Calculate the amount of fuel used in this trip, assuming it is much less than the total mass of the train.

(c) Calculate the amount of water used during this trip, assuming that this, too, is much less than the mass of the train.

PROBLEM 20.

Each member of a family of 4 opens the refrigerator 8 times a day. Every time it is opened, 75% of the 1 m^3 of air in the refrigerator is replaced by air from the room. In addition to the air, the refrigerator contains different things, equivalent to 200 liters of water. The temperature inside the refrigerator is 2C, the room is 20C. No heat leaks out when the door is closed. The refrigerator is cooled by an ideal Carnot machine. The vapor pressure of water at 20C is 0.1 atm, at 2C it can be ignored. The heat of vaporization of water is 2.26 MJ/kg. R = 8.31 J/Kmole. A mole of gas occupies 22.4 liters at 0C.

(a) What are the molar heat capacities c_V and c_p for air?

(b) What is the average power needed to operate the refrigerator when the air in the house is dry?

(c) What is the average power needed to operate the refrigerator when the air in the house is saturated with water vapor?

PROBLEM 21.

The heat capacity of a solid is $C = AT^3$, where A is a constant. This solid is the low temperature reservoir of a reversible refrigerator. The high temperature reservoir is at room temperature. The solid is cooled from room temperature to almost absolute zero.

(a) Find an expression for the amount of work required to cool this solid.

(b) What is the decrease in entropy of the solid?

(c) What is the decrease in internal energy of the solid?

(d) What are the increases in entropy and internal energy of the high temperature reservoir?

PROBLEM 22.

The equation of state of an imperfect gas is given by $p = \frac{N}{V} RT \left(1 + B(T)\frac{N}{V}\right)$ where $B(T)$ is some function of the temperature. This gas undergoes a small isothermal expansion ΔV at constant N. The amount of heat going into the system is ΔQ.

(a) Relate ΔQ to ΔV, keeping only linear terms.

(b) Evaluate the partial derivatives in (a).

(c) Interpret the result.

PROBLEM 23.

A well insulated steel tank has volume V. The tank contains air at pressure p_1 and temperature T_1. It is attached to a compressed air line which supplies air at steady pressure p' and temperature T'. Initially the valve between the tank and the line is closed. The valve is then opened long enough to change the pressure in the tank to p_2, and it is then closed again.

Show that in transport of this kind the energy balance is given by $N_2(u_2 - h') - N_1(u_1 - h') = Q$, where u is the molar internal energy, h' is the molar enthalpy h'=u'+p'v' where v' is the molar volume occupied by air in the line, and Q is the heat added to the air.

How many moles N_2 are in the tank at that moment, and what is the temperature T_2?

Assume that (1) the tank and the air are always at the same temperature, (2) Air is a perfect gas with molar specific heats $c_p = \frac{7}{2}R$ and $c_V = \frac{5}{2}R$.

For numbers use $V_1 = 20m^3$, $p_1 = 1bar$, $T_1 = 22C$, $p' = 5bar$, $T' = 30C$, $p_2 = 3bar$. The mass of the steel tank is m_t 1000 kg, the heat capacity of steel c_s is 100 cal/kg/K and the gas constant is R=8.3 x $10^{-5}m^3$ bar/mole/K.

PROBLEM 24.

A thermodynamic model for gravitational collapse can be constructed by adding the gravitational self energy to the ideal gas. A spherical mass M of a cloud of dust with radius R has gravitational energy $U_g = -\frac{3M^2G}{5R}$.

(a) Find the equation of state of the cloud.

(b) Find an expression for the isothermal compressibility.

(c) Discuss the conditions under which the cloud is no longer thermally stable.

PROBLEM 25.

The heat capacity at constant pressure for a certain solid is γT with $\gamma = 5 mcal/degree^2/mole$. At T=300K the solid changes into a classical ideal gas which is kept at constant pressure. The heat of this transition is 150 cal/mole. The entropy of this gas at T=600K is 5.5 cal/degree/mole. Is this gas mono-atomic or diatomic? Use R=2cal/degree/mole.

PROBLEM 26.

A substance has the following properties:

(I) The amount of material is fixed at N moles.

(II) At constant temperature T_0 the work W done by it on expansion from a volume V_0 to a volume V is

$$W = NRT_0 \ln(\frac{V}{V_0})$$

(III) The entropy is given by

$$S = NR\frac{V_0}{V} \left(\frac{T}{T_0}\right)^x$$

In these expressions T_0, V_0, and x are fixed constants.

(A) Calculate the Helmholtz free energy of the system.

(B) Find the equation of state for the pressure p in terms of V, T, and N.

(C) Find the work done on expansion at constant T, where T is arbitrary.

PROBLEM 27.

The heat capacity at constant pressure is given by

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_p$$

and the coefficient of thermal expansion is given by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

The amount of material N is always kept constant.
If we consider $S(T, p)$ we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

(A) Show that this leads to

$$TdS = C_p dT - \alpha TV dp$$

One can show that (but you do NOT have to!)

$$\lim_{T \to 0} \frac{\alpha V}{C_p} = X$$

where X is a finite constant.

(B) Show that this has the consequence that in an adiabatic process one can never reach $T = 0$ by a finite change in pressure.

PROBLEM 28.

A container of volume V_0 is divided into two equal parts by a removable wall. There are N_0 moles of gas in equilibrium at temperature T_i on the left, the right side is empty. The container is isolated, no heat goes through. The internal wall is suddenly removed and the gas can expand freely until it finally fills up the whole container.

(A) Is the gas in equilibrium just after the wall has been removed?

(B) Is the free expansion a reversible process?

(C) Does the entropy of the gas increase, decrease, or stay the same?

(D) Does the energy of the gas increase, decrease, or stay the same?

Assume that we have a different, reversible process that brings a gas at constant internal energy from a temperature T_i and volume $\frac{1}{2}V_0$ to a volume V_0 and temperature T_f. At each stage of this reversible process the gas is described by an internal energy function of the form $U = u(T, V, N)$.

(E) Is this reversible process adiabatic?

(F) Express the response function $\left(\frac{\partial T}{\partial V}\right)_{U,N}$ in terms of partial derivatives of the energy function $u(T, V, N)$.

(G) A mono-atomic ideal gas has $u(T, V, N) = \frac{3}{2} NRT$. How much does the temperature change in a free expansion from volume $\frac{1}{2} V_0$ to V_0?

PROBLEM 29.

Under adiabatic compression a gas changes its temperature when the pressure is changed, in a reversible manner. The response function describing this situation is $\Omega = \left(\frac{\partial T}{\partial P}\right)_{S,N}$.

Show that $\Omega = \frac{TV\alpha}{C_p}$ with $\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N}$ and C_p the heat capacity at constant pressure.

For an ideal mono-atomic gas $\alpha T = 1$ and $C_p = \frac{5}{2} NR$. Find the function f defined by $T = f(p)$ in this adiabatic process.

PROBLEM 30.

The Jacobian J is defined by

$$J(x, y; u, v) = \frac{\partial(x, y)}{\partial(u, v)} = \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v$$

Show that $J(T, S; p, V) = 1$.

PROBLEM 31.

A fluid undergoes an *adiabatic throttling process*. This means that the fluid is pressed through a porous plug, with initial pressure p_1 and final pressure p_2.

(A) Show that the enthalpy of the fluid is constant in this process.

As a result of this process, the temperature changes (remember when you pump air in your bicycle tire, or when you let the air escape?). The amount of change is measured by the *Joule-Thomson coefficient* η_{JT}, defined by

$$\eta_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$$

(B) Show that $\eta_{JT} = \frac{V}{C_p}(T\alpha - 1)$

(C) What is the value for an ideal gas?

Chapter 3

Phase transitions.

3.1   Phase diagrams.

What happens when I suddenly change my state dramatically?

STUDY OF RELATIONS.

In the previous two chapters we have studied the mathematical description of thermal systems, i.e. systems which have a large number of internal degrees of freedom. We found the existence of many relations between reversible changes in in state variables. Note that the study of irreversible changes is much harder, but certainly not less important. That is for a different course, however.

ENTROPY.

The fundamental question in thermodynamics is: *What is entropy*? Is it simply a quantity that represents the energy stored in the internal degrees of freedom, or is it more? This question can not be answered in thermodynamics, and we have to apply statistical mechanics to obtain one possible answer. In thermodynamics we simply use entropy as a state variable, and find ways to measure it.

CONSEQUENCES OF RELATIONS.

Based on the laws of thermodynamics and the mathematics of functions of many variables we were able to draw some very strong conclusions about response functions and stability. The relations between response functions have

important technical consequences. For example, if we try to design a material with a large coefficient of thermal expansion α we know that we always have $\alpha^2 TV = \kappa_T(C_p - C_V)$ and hence the right hand side should be large. But in a solid $C_p - C_V$ is always small and hence we need a material with a large isothermal compressibility! And then the next question is: does that have negative consequences for the applications of our new material?

DISCONTINUITIES.

In this chapter we will focus on another important general aspect of the equations of thermodynamics. We will investigate the effects of discontinuities in the equations of state. These discontinuities manifest themselves in the physical world as phase transitions. What happens when a material abruptly changes its properties?

What is the most important phase transition in the world?

For example, zirconia is a very important ceramic material. It has a high melting point, is very hard, and is inert. In short, it is very useful in many applications. The problem, however, is that at around 1100 centigrade zirconia transforms from a tetragonal high temperature phase into a monoclinic low temperature phase. This transition is very disruptive, and fractures the material. The more we know about what happens at this phase transition, the more we can control it and make the consequences more benign.

PRACTICAL IMPORTANCE.

The study of phase transitions is of enormous practical importance. When does a material become superconductive? How does magnetism change? In this and the following chapters we will study phase transitions from a macroscopic point of view. This is important, because this relates directly to the way phase transitions are observed. In order to explain why phase transitions happen, however, we need to look at the microscopic nature of the material, and hence those answers are only found in statistical mechanics. Nevertheless, again thermodynamics will provide us with important boundary conditions that all materials will have to obey.

MODEL SYSTEM.

In order to make the discussion less cumbersome, we will consider a model system in which the only relevant state variables are $\{p, V, \mu, N, S, T\}$. There is only one material present. These restrictions are, however, not essential, and other systems can be discussed in a similar way. If we ignore chemical reactions

and their influence on phase transitions, *we can assume that the amount of material, N, is fixed.* The three state variables which are easiest to change and control are the pressure p, the volume V, and the temperature T. Since we already prescribed the value of N, only two of the variables in the set $\{p, V, T\}$ are independent. Since N is an extensive variable, we can choose any combination of two variables from $\{p, V, T\}$. Systems like this are called pVT systems. Note that we assume that the system is in equilibrium, else equations of state like $p = f(V, T)$ would not exist.

PHASE DIAGRAM.

The variables p and T are intensive variables, and their values are chosen by bringing the system in thermal and mechanical contact with appropriate reservoirs of pressure p and temperature T. From an experimental point of view, these are good handles on the system, and often easy to use. These reservoirs are infinitely large systems in thermodynamic equilibrium. Any choice for the values of p and T is possible, and hence we can give our model system arbitrary values of the pressure and temperature. Of course, we assume positive values for both p and T. Hence for any combination of p and T we are able to specify the volume and all other aspects of the system. The system is represented by a plot in the p-T diagram, called a phase diagram. A very general phase diagram looks like figure 3.1. The solid lines indicate phase boundaries. Crossing such a line in the p-T diagram will cause a jump in the value of the volume, and in the values of other extensive state variables. Sometimes the jump is only in the value of the derivatives, though. Most simple pVT systems have a phase diagram of the form shown in figure 3.1.

Give an example of a solid to gas transition.

ANATOMY OF A PHASE DIAGRAM.

The solid lines separate the well-known phases of most materials. At low temperature and high pressure the system is in a solid state. At higher temperature it either becomes a gas or a liquid. At the phase boundary the two phases can coexist. The points t and c are special. At the triple point t all three phases can coexist. At the critical point c the phase boundary between liquid and gas vanishes. The phase boundary between solid and liquid never vanishes, at least as far as we know. This implies that gas and liquid are more alike than gas and solid, which makes sense intuitively.

CRITICAL POINT.
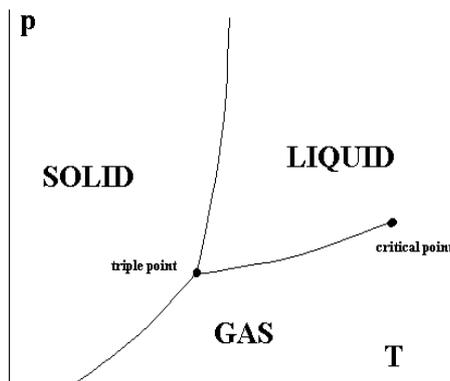
Figure 3.1: **Model phase diagram for a simple model system.**

The interpretation of a critical point is as follows. If the temperature is in the range (T_t, T_c), an increase in pressure will cause a phase transition between two states. At low pressure the state of the system resembles a gas, at high pressure a liquid. Since these two states are separated by a phase transition, we can clearly identify them. If the temperature is above T_c, however, this clear separation vanishes. At low pressure the system still behaves like a gas, and at high temperature like a liquid. The change from one to the other is continuous and it is not possible to uniquely identify where we change from one type of behavior to another. This continuous change is not possible from liquid to solid, as far as we know from experiments.

CRITICAL POINTS IN A SOLID.

A famous example of a critical point in a solid is the α to γ phase transition in solid Ce. The phase diagram looks like figure 3.2. If we cool Ce at atmospheric pressure we have to go through the phase boundary, and the volume changes in a discontinuous manner. If the whole material were uniform, this would not give any problems. But any imperfections in the material cause some parts of the material to transform before other parts, causing large strains in the material. As a result, large single crystals of α-Ce are hard to make. The solution to this problem is to go around the critical point. First increase the pressure, than decrease the temperature, and finally decrease the pressure again.

ENERGY CONSIDERATIONS.

At a phase boundary two distinct phases of the material can coexist. This is only possible if these two phases have the same energy at the phase boundary. If not, one phase would be preferred. The question is, which energy plays a
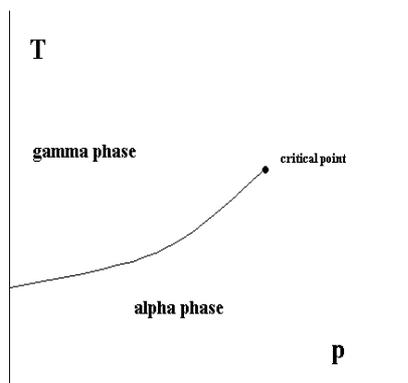
Figure 3.2: **Phase diagram for solid Ce.**

role. Since the phase boundary is determined by specific values of p and T, and since N is kept constant, the energy of interest is the Gibbs energy $G(T, p, N)$. Therefore, for a path in p-T space crossing a phase boundary, the Gibbs free energy is continuous, but its derivatives are not. The reason for this is that the Gibbs free energy is minimal as a function of all internal parameters at a given value of p and T. The internal parameters define the phase we are in. Therefore phase transitions are found by studying singular behavior in the derivatives of the Gibbs free energy.

DISCONTINUITY IN THE VOLUME.

The Gibbs energy is continuous at a phase boundary. If the Gibbs free energy were not continuous at a phase boundary, a picture of the Gibbs energy as a function of pressure would look like figure 3.3 for example (note that $\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N} \leq 0$ because of stability). One could then follow the lower branch across the phase boundary, and have a state of lower energy, which by definition would be the stable state. This would simply indicate that we marked the phase boundary at the wrong place. Hence the Gibbs free energy as a function of pressure at constant temperature and N looks like 3.4.

Once we have the Gibbs energy as a function of pressure, the volume follows automatically through $V = \left(\frac{\partial G}{\partial p}\right)_{T,N}$ and this is shown in figure 3.5. First of all, because of the curvature of the Gibbs free energy the volume decreases with pressure. Second, at the phase transition the volume jumps down in a discontinuous manner, it never jumps up.

Is it possible for the volume to be continuous as a function of pressure at the phase transition?
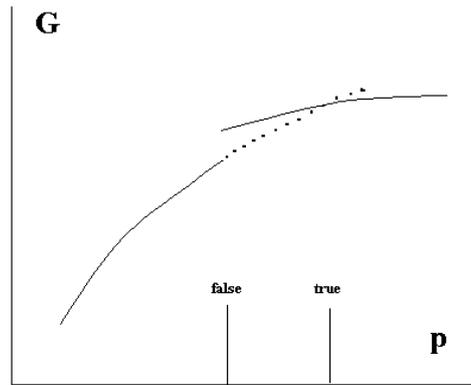
Figure 3.3: **Gibbs energy across the phase boundary at constant temperature, wrong picture.**
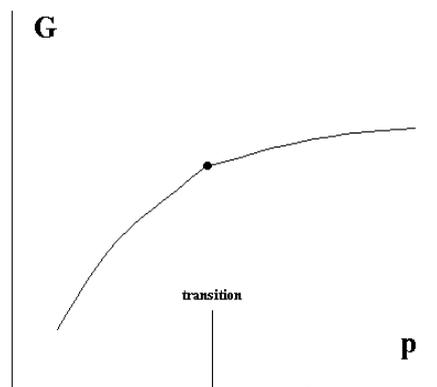
Figure 3.4: **Gibbs energy across the phase boundary at constant temperature, correct picture.**
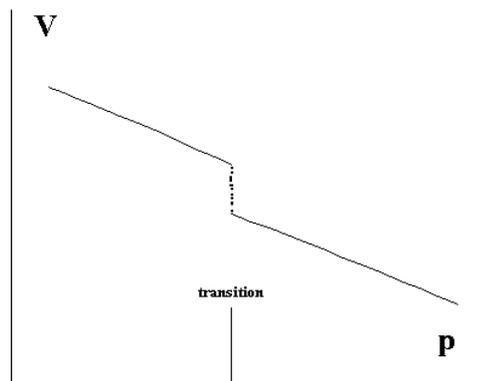
Figure 3.5: **Volume versus pressure at the phase transition.**

Is it possible for the volume to decrease as a function of temperature at a phase transition?

OTHER PICTURES OF THE PHASE TRANSITION, VT DIAGRAM.

In the V-T plane this phase diagram looks like figure 3.6. In this diagram we see regions which are not accessible, because the volume of the system jumps at the phase boundary. There is no continuous path from the solid phase to the others, but there is a continuous path from liquid to gas, around the critical point. Inaccessible regions only show up in diagrams when extensive state variables are involved. What happens when the system is prepared at a given volume V_0 at a high temperature and then cooled down to a temperature which would force the state of the system to be in an inaccessible region? The answer is simple, the system will phase separate. Part of it will have a small volume, part of it a large volume, and both phases are in equilibrium with each other. The amount of each phase is determined by where in the inaccessible region the point (T, V_0) is situated.

PHASE SEPARATION ANALYZED.

As an example, consider that the system has volume V_c and is cooled down at constant volume to a temperature T below T_c, but above T_t. The volume per mole (specific volume) of the gas and the liquid at this temperature and at a pressure p are $v_g(p, T)$ and $v_l(p, T)$. Because gas and liquid will be in equilibrium, they will be at the same pressure. We need to determine the amounts of material N_g and N_l in the gas and liquid phase. We obviously have:
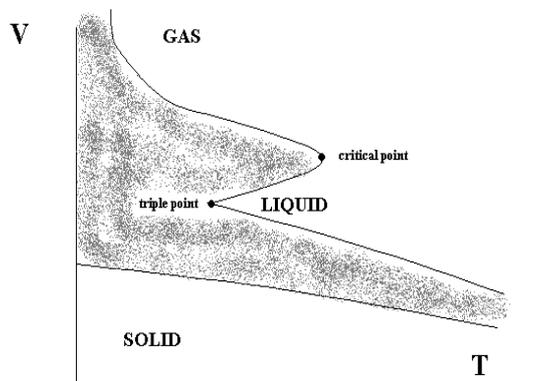
Figure 3.6: **Model phase diagram for a simple model system in V-T space.**
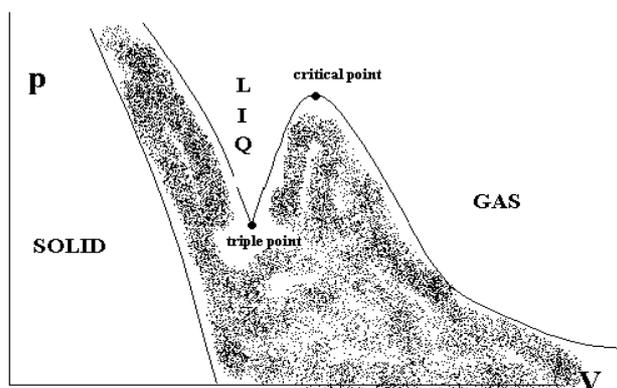
Figure 3.7: **Model phase diagram for a simple model system in p-V space.**

$$N = N_g + N_l \tag{3.1}$$

and

$$V_c = N_g v_g(p, T) + N_l v_l(p, T) \tag{3.2}$$

This seems to be incomplete, but we have to keep in mind that the pressure is determined from the phase diagram 3.1. Hence we know exactly how the system phase separates.

The same system in a p-V diagram looks like figure 3.7. Notice again the forbidden regions. It is also possible to draw the three dimensional surface $V(p, T, N)$ for fixed N, but that is beyond my capabilities and artistic talents.

3.2 Clausius-Clapeyron relation.

So far we made some general statements about what is happening at a phase boundary. Our next task is to give a more quantitative description of the phase boundaries. Thermodynamics limits the freedom we have in drawing phase diagrams!

BASIC ENERGY.

What is the best way to describe mathematically what is happening? Since in terms of p and T all values of these state variables are possible, we will use the pressure and temperature as independent variables. The free energy in this case is the Gibbs potential $G = U - TS + pV$. The Gibbs free energy is a minimum as a function of all internal parameters when p, T, and N are fixed. Hence the state with the lowest Gibbs free energy is stable in a p-T diagram. In our simple system the Euler relation tells us that $G = \mu N$. Since N is fixed, the chemical potential in this case is equal to the Gibbs free energy per mole, and is often used in stead of the Gibbs free energy in this case. To be precise, however, we will use the Gibbs energy as our basic energy.

PHASE BOUNDARY.

In order to determine the phase boundary between to phases we need an analytical form of the Gibbs free energy for both phases. Assume that we have expressions for this energy in each phase, which we can extend to all values in p-T space by analytic continuation. The phase boundary then follows from

$$G_1(p, T, N) = G_2(p, T, N) \tag{3.3}$$

and since N is fixed, this yields an equation $p = p_{co}(T)$ for the pressure as a function of temperature. This relation describes the <u>coexistence curve</u> of the two phases.

The slope of the Gibbs free energy as a function op pressure is equal to the volume, $\left(\frac{\partial G}{\partial p}\right)_{T,N} = V$, and hence as a function of the pressure the Gibbs free energy is always increasing (volumes are positive by definition). The second order derivative of the Gibbs free energy with pressure is equal to $\left(\frac{\partial V}{\partial p}\right)_{T,N}$, and is always negative because of stability requirements. Therefore the slope of the Gibbs free energy as a function of pressure is decreasing. A picture of the Gibbs free energy of the two phases which we study might look like the figure 3.8. The lowest curve gives the stable state for each value of the pressure. At the phase transition the slope of the Gibbs free energy jumps to a smaller value, and hence the volume jumps to a smaller value.
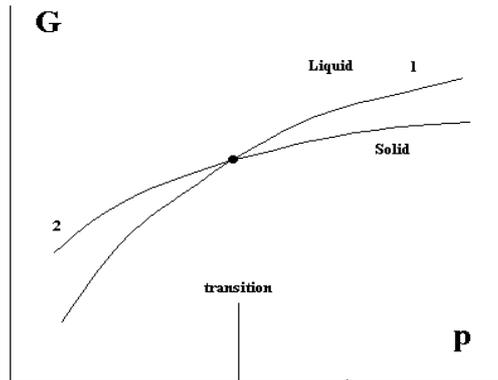
Figure 3.8: **Gibbs energy across the phase boundary at constant temperature for both phases.**

In a picture of volume versus pressure, why can the volume not have the same value for two different values of the pressure.

FOLLOWING THE COEXISTENCE CURVE AT BOTH SIDES.

The differential for the Gibbs free energy is given by

$$dG = V dp - S dT + \mu dN \tag{3.4}$$

but since N is constant, the last term is zero. The partial derivatives of the Gibbs free energy give us V(p,T,N) and S(p,T,N) for both phases. If we are at a point on the coexistence curve, and make small changes in the temperature and pressure in such a manner that we remain on the coexistence curve, the Gibbs free energy of the two phases remains the same (by definition), and hence along the coexistence curve we find:

$$V_1 dp - S_1 dT = V_2 dp - S_2 dT \tag{3.5}$$

or

$$\left(\frac{dp}{dT} \right)_{co} = \frac{S_1(p,T) - S_2(p,T)}{V_1(p,T) - V_2(p,T)} \tag{3.6}$$

which is the famous Clausius-Clapeyron relation. The pressure and temperature on the right hand side are related by $p = p_{co}(T)$. Both the numerator and the denominator on the right hand side are often divided by N, yielding a ratio of differences in molar volume and molar entropy.

LATENT HEAT.

The <u>latent heat</u> of a phase transformation is the amount of heat needed to transform the system at a given pressure and temperature along the coexistence curve completely from one phase to the other. The latent heat is positive if we transform material from a low temperature phase to a high temperature phase. We indeed need energy to melt ice and boil water! The fact that the latent heat is positive is easy to prove, similar to how we showed that the volume decreases when we go to higher pressure. In the previous chapter we saw that $\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} \leq 0$ and hence the picture of G versus T looks qualitatively like figure 3.8. Since $S = -\left(\frac{\partial G}{\partial T}\right)_{p,N}$ a decrease in the slope of G versus T is a jump down in the value of -S and hence an increase in S.

The latent heat is denoted by $L_{1\rightarrow 2}(T)$ for the process going from phase 1 to phase 2 at a temperature T and a corresponding value of the pressure along the coexistence curve. Since heat is related to changes in the entropy, we have

$$L_{1\rightarrow 2}(T) = T\left(S_2(p_{co}(T), T, N) - S_1(p_{co}(T), T, N)\right) \tag{3.7}$$

and the Clausius-Clapeyron relation takes the form

$$\left(\frac{dp}{dT}\right)_{co} = \frac{l_{1\rightarrow 2}(T)}{T(v_2(p,T) - v_1(p,T))} \tag{3.8}$$

where we use the lower case characters to indicate the molar volume and molar latent heat (i.e. the quantities are per mole).

CONSEQUENCE FOR PHASE BOUNDARY.

The Clausius-Clapeyron relation 3.6 is still in its general form. Note that if 2 denotes the high temperature phase, both the numerator and the denominator are positive. Hence the coexistence curve $p_{co}(T)$ always has a positive slope!

EXAMPLE.

As a specific example take the transition from liquid to gas. In this case the volume of the liquid is much smaller than the volume of the gas and can be ignored. Using the ideal gas law gives:

$$\left(\frac{dp}{dT}\right)_{co} \approx \frac{p_{co}(T)l_{1\rightarrow 2}(T)}{RT^2} \tag{3.9}$$

In many cases the latent heat is only very weakly temperature dependent. In that case we can do the integration and obtain

$$p_{co}(T) \approx p_0 e^{\frac{l_{1\rightarrow 2}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} \tag{3.10}$$

which indeed has a positive slope. This is a useful formula for a number of applications. The limit T$\to \infty$ of $p_{co}(T)$ is finite. Consequently, this relation does not hold for the complete solid-liquid coexistence curve (but might be close for part of it). For such a phase boundary we need to take the values of the volumes of both phases into account. Also, this relation does not hold near a critical point, where the latent heat goes to zero, and the molar volumes become equal.

To continue the study of this example, consider a closed volume V containing N moles of water. The temperature T is the control variable. If we are at room temperature, and the volume is chosen in such a manner that the pressure is around atmospheric pressure, we will see water at the bottom, an interface, and vapor at the top.

Which implicit assumption did we make?

This system lends itself to an easy experiment. By measuring the level of the interface, we can determine the volume of the liquid and gas, V_l and $V_g = V - V_l$. By doing some optical absorption measurement we can determine the density of the vapor and hence we find the amount of vapor N_g and hence we know the amount of water $N_l = N - N_g$. If the gas can be described by the ideal gas law, we find $p_{co}(T) = \frac{N_g RT}{V_g}$.

Up or down or what??

What happens if we increase the temperature? Will the interface go up or down? The answer is, that depends on the volume V. The relative volumes of the liquid and gas phase follow from

$$V = N_l v_l(T, p_{co}(T)) + N_g v_g(T, p_{co}(T)) \tag{3.11}$$

for all temperatures as long as we are below the critical temperature T_c. If the volume is larger than the critical volume V_c the phase diagram 3.6 shows that at some temperature below T_c all material will be vapor, and hence we see the interface drop to the bottom of the container. If the volume V is less than the critical volume V_c, on the other hand, all material will transform to liquid, and the interface will actually rise! This seems counter-intuitive. How can we increase the temperature and see more liquid form? The answer is found in the fact that the total volume is constant, and that the increase in temperature comes with an increase in pressure which is sufficient to condensate the vapor into liquid if the volume is small enough (i.e. smaller than V_c).

What happens if $V = V_c$? In this case the interface does not go to the top or the bottom of the container, but remains somewhere in the middle. So what happens when T reaches T_c. The interface is supposed to disappear, and it does

indeed. If we reach T_c in this experiment, the properties of the liquid phase and the vapor phase become more and more similar, and at the critical interface they are identical. We only see the interface between water and vapor because the index of refraction is different in the two phases. At the critical point the indices of refraction become identical, and the interface disappears from our view. The same holds for any type of measurement.

3.3 Multi-phase boundaries.

At the triple point in the phase diagram three phases coexist, and hence the equations determining the triple point are

$$G_1(p, T, N) = G_2(p, T, N) = G_3(p, T, N) \qquad (3.12)$$

Since the total amount of material is fixed, there are two equations for two unknowns. In general, this set of equations has one unique solution. Therefore, we only find one triple point.

CRITICAL POINT.

It is also easy to see that in general we have only one critical point. The coexistence line is determined by one equation for the free energy, and the critical point also states that a parameter like the volume has to be the same. In this case the simultaneous equations are $G_1(p, T, N) = G_2(p, T, N)$ and $V_1(p, T, N) = V_2(p, T, N)$.

QUADRUPLE POINT.

Suppose in our model system we would have four different phases. The solid could, for example, change its structure at a certain temperature, or become magnetic. Would it be possible to have all four phases coexist? The answer is clearly no for our simple case. Since the only two independent variables are p and T, the set of three equations determining this special point is over-complete and in general no solution exists. If we want to solve three simultaneous equations, we need three independent variables. One could allow N to change by bringing the system into contact with a reservoir of constant chemical potential. This is not possible, however, since in that case the system would be described by the set of state variables $\{p, T, \mu\}$ and these are all intensive. Therefore, we have to introduce another state variable. For example, take a (possibly) magnetic system with total magnetic moment M. For simplicity, we assume that the direction of this moment is not important. The corresponding intensive state variable is the magnetic field H. In this case our system is described by the four variables $\{p, T, H, N\}$ and we now use the modified, magnetic Gibbs free energy

$$\mathcal{G}(p, T, H, N) = U - TS + pV - HM \qquad (3.13)$$

which is still equal to μN, since we now have to add one term to the Euler relation. A point where all four phases coexist is now described by certain values $\{p_q, T_q, H_q\}$ and if such a quadruple point exists, it needs in general a non-zero applied magnetic field. Note that we ignored the energy stored in the field (see previous chapter). This energy is independent of the particular phase, however, and cancels in the equations.

MULTI-COMPONENT SYSTEMS.

If M+1 phases coexist for a certain system, we need to solve M equations. The number of unknowns cannot be smaller than M. Hence we arrive at the general conclusion that

The number of phases which can coexist for a system described by M independent intensive state variables is at most equal to M+1.

For example, we have a system with r different types of material, with number of moles N_i, $i = 1 \ldots r$, for each type. Assume that the total amount of material is fixed, hence we have something like $\sum w_i N_i = N$ is constant, where the weights w_i depend on the chemical reactions that are described. In that case, using also p and T as variables, we have r+1 independent variables that can change, and hence we have at most r+2 phases that can coexist at one time.

APPLICATION TO CHEMICAL REACTIONS.

In a chemical experiment one might look at reactions between two species A and B, according to $A + B \leftrightarrow AB$. The total amount of moles of A and B, either free or combined, are fixed. The relative number can change. Therefore, this only leaves one state variable to describe the state of the reaction, and we could take this variable N_{AB}, the number of molecules AB. It is better to use the corresponding chemical potential μ_{AB}, however, since that is in general the state variable which is controlled in chemical experiments. The other state variable we can easily vary is the temperature T. Since there are two independent state variables, at most three phases can coexist. One phase is easily identified as A and B free, the other as A and B bound in AB. Requiring these two phases to coexist eliminates one independent state variable, and leads to an equation for the coexistence curve of the form $N_{AB}(T)$. Hence the state of the reaction is completely determined by the temperature. If we also allow the AB material to solidify, we introduce a third phase. The AB material is either in solution or precipitated out. There is only one temperature T_t at which all three phases coexist. Interesting problems arise when one assumes that only the AB molecules in solution are able to dissociate within the time of the experiment. An efficient reaction path then often requires manipulating both μ_{AB} and T to obtain a complete reaction.

3.4 Binary phase diagram.

Basic variables.

A very important application is found in binary phase diagrams. Suppose we have two materials, A and B, and each can dissolve in the other. Suppose we have N_A moles of material A with B dissolved in it, and N_B moles of material B with A dissolved in it. Since material cannot disappear, we have $N_A + N_B = N$ is constant. Therefore, at most four phases can coexist at a given time. In these solid solutions we typically work at atmospheric pressure, however, which for practical purposes is almost equal to zero (for solids!!) and which therefore can be ignored. The variables that can be changed easily are the temperature T and the fraction of material B in the total material, c_B, which is the ratio of the amount of pure material B (without any A dissolved in it) to N. In such a phase diagram at most three phases can coexist.

Nature of c_B.

Although the variable c_B is intensive, it is only so because we divided by N to get a density. The variable c_B really measures an amount of material, and really plays the role of an extensive state variable. The true intensive state variable would be the corresponding chemical potential, but that one is hard to control directly in alloys. Just as we saw in the VT diagram, we will have regions in the c_BT diagram which are not allowed, which do not correspond to states of the system.

Typical phase diagram.

A typical phase diagram for a binary alloy looks like figure 3.9. The curvature of the phase boundaries is always the same, and can be derived from stability criteria. At low temperatures, for very low or very high concentrations c_B of B we have one type of material. If the concentration of B is in between, the material will phase separate into regions rich in B, consisting of B(A) material where A is dissolved in B, and regions poor in B, consisting of A(B) material. The division between these can easily be calculated if we know where the phase boundaries are. We use a similar lever rule as we used for the volumes earlier in this chapter. At higher temperatures the system is either liquid, pure material, or a mixture of liquid and pure material. There is exactly on temperature and concentration where all three phases can coexist. This point is called the eutectic point.

Crossing the line.
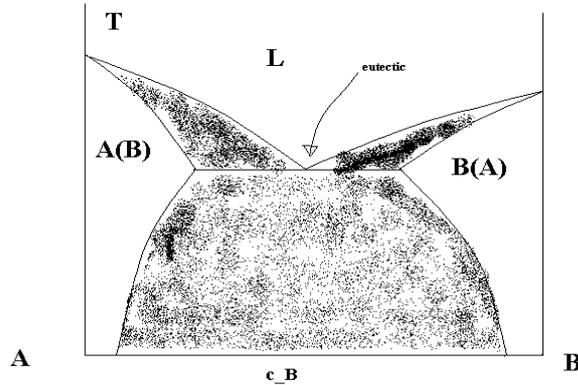
Figure 3.9: **Typical binary phase diagram with regions L=liquid, A(B)=B dissolved in A, and B(A)=A dissolved in B.**

Suppose we prepare a liquid at high temperature containing both elements A and B and the concentration of B is C_B^0 is low. We now cool the mixture and end in a stable region of material A(B). What happens in between and what is the result of our experiment? In order to describe this, see figure 3.10.

When we reach the upper boundary of the forbidden region, we have an equilibrium of solid material with a concentration of B of C_L and liquid with the original concentration. When we lower the temperature, more solid will form, and the concentration of the solid phase will increase. But since we form more solid with too small an amount of B, the concentration of B in the liquid will also increase. Near the lower boundary of the forbidden region we have mainly solid material with almost the original concentration of B and some liquid with a high concentration of B material. Since no material is lost, we can easily find the amounts of material N_l in the liquid phase and N_s in the solid phase:

$$N_s(c_B^0 - c_1) = N_l(c_2 - c_B^0) \tag{3.14}$$

This rule is called the lever rule.

In the scenario described above we have made one basic assumption, that *the system is always in thermal equilibrium!* In other words, we assume that the process is infinitely slow. What are the time scales involved? First of all, the cooling time. The second time scale is related to the diffusion of material B in the liquid and in the solid. The last one is the limiting factor, and this time can be long. In addition, in order for the solid to start forming we need initial seeds (nucleation of material). In many cases, this is not a limiting factor.

Suppose we cool the material and grains of solid form. Suppose that the diffusion of B material is fast, and we end up with only grains of solid with the correct composition. Since we are now dealing with a solid, most likely we will have empty space in between the grains! If the original melt had some
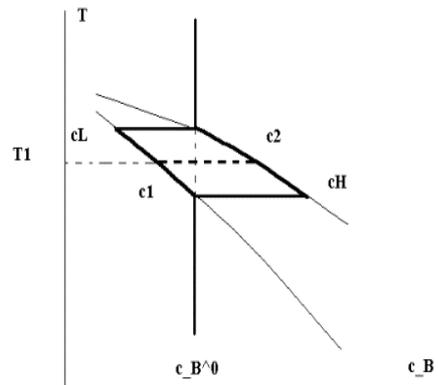
Figure 3.10: **Solidification in a reversible process.**

impurities, it is possible for these impurities to collect in these empty spaces. In general, the material at the grain boundaries will have a lower density and the volume of the resulting material is too large. What can we do about that? If the material is a metal, we can roll it and press it to get rid of these empty spaces. For ceramics, that is much harder.

But that is not all folks. Typically, the diffusion of B material in the solid is incomplete. Therefore, the grains will have a concentration gradient. The centers are poor in B material. Near the grain boundaries we have more or less the correct concentration. The excess of B material will be in between the grains! What to do now? Since there is a concentration gradient, there is a difference in chemical potential, and there is a driving force which wants to make the concentration uniform. Since the diffusion is always much better at higher temperature, we want to keep the solid at a temperature just below the lower bound for a while. This annealing process is very important when making materials. Sometimes the times involved are quite long. Sometimes other tricks have to be applied during the anneal.

The previous discussion shows that phase transitions in solids are quite difficult to deal with. That is why we deal with gas to liquid transitions in most of this chapter. In the next chapter we will discuss magnetic phase transitions, which also are much easier to deal with. Nevertheless, a study of phase transitions in solids is of great practical importance! Just talk with your mechanical engineering friends.

EUTECTIC POINT.

The eutectic point is of great practical importance. Opposed to the gas-liquid coexistence, phase separation at low temperatures is a very slow process, since it involves atomic motion in a solid. It is therefore possible to create meta-stable materials in the forbidden regions by cooling a sample very rapidly. Typically
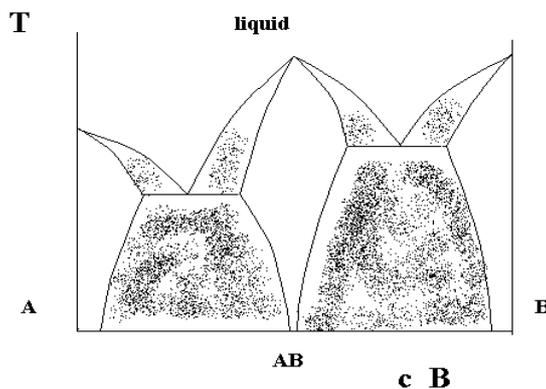
Figure 3.11: **Typical binary phase diagram with intermediate compound**
AB**, with regions L=liquid, A(B)=B dissolved in A, B(A)=A dissolved in**
B, and $AB= AB$ **with either A or B dissolved.**

this is done by dropping a drop of liquid into cold water. If we are not at the
eutectic point, it is almost certain that small amounts of material A(B) or B(A)
will form during cooling (when we go through the top forbidden regions) and
the final material will not be homogeneous. If we are at the eutectic point, this
region where material separates is reached at the lowest possible temperature
(making the process the slowest), furthest from the stable phases (increasing
the energy needed for the process). Meta-stable materials at a concentration
corresponding to the eutectic point are therefore easiest to prepare.

INTERMEDIATE COMPOUNDS.

In many cases there are stable compounds of the materials A and B present,
and the phase diagram then looks different. A typical example is figure 3.11
where we included a stable material AB . The overall structure and interpre-
tation is the same, except that we now have a region of AB material in which
either A or B is dissolved. Quite often the range of stability of the intermediate
compound is very small, so small that it collapses to a single line in the diagram,
see figure 3.12. An example of an impossible phase diagram is figure 3.13, where
we have four phases coexisting at one point.

3.5   Van der Waals equation of state.

MORE QUANTITATIVE APPROACHES BASED ON ENERGY.

The previous discussion of phase transitions was very general. In order to
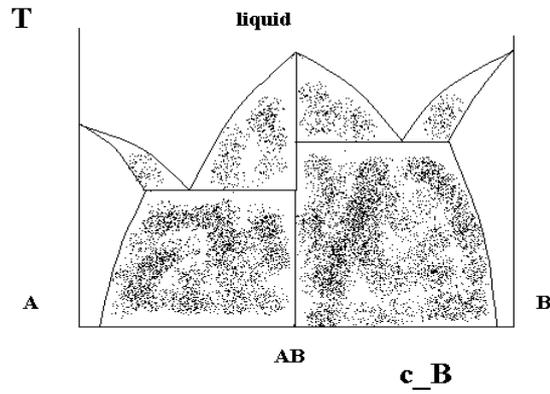
Figure 3.12: **Typical binary phase diagram with intermediate compound** AB**, where the intermediate region is too small to discern from a line.**
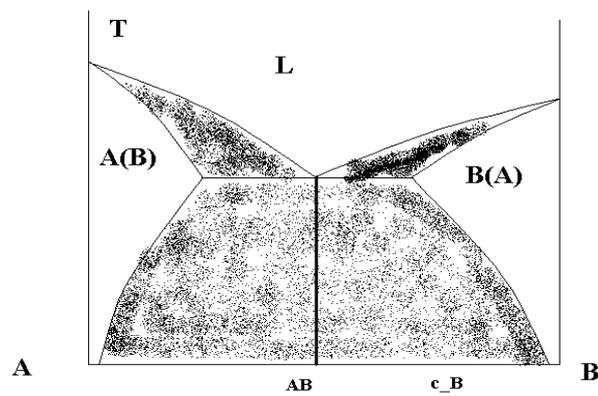
Figure 3.13: **Impossible binary phase diagram with intermediate compound** AB**, where the intermediate region is too small to discern from a line.**

give details we need to assume a certain form for the energy as a function of the state variables. Energy is the most basic thermodynamic state variable for which we can develop models that can easily be interpreted. This will be done in the next chapter.

MORE QUANTITATIVE APPROACHES BASED ON EQUATIONS OF STATE.

In a p-V-T system the three state variables which are easily controlled or measured are the pressure p, the volume V, and the temperature T. We assume that the number of particles N is again fixed, and hence of the three variables $\{p, V, T\}$ only two are independent. A mathematical relation describing this dependency, an equation of state, is needed to show how they are related. The ideal gas law, $pV = NRT$, is the easiest example of such an equation of state, but unfortunately a system obeying the ideal gas law does not show any phase transitions. An ideal gas is an approximation of a real gas, and describes a real gas in the limit of very low densities. Therefore, an attempt to improve upon the ideal gas law would be to assume an equation of state of the form

$$\frac{p}{RT} = \sum_{j=1}^{\infty} B_j(T) \left(\frac{N}{V}\right)^j \tag{3.15}$$

with $B_1(T) = 1$. The value of this first term is determined by the requirement that in the low density limit the ideal gas law should be obtained. This expansion is called a virial expansion and is the basis for many attempts to describe a real gas by some kind of perturbation theory.

VALIDITY OF EQUATIONS OF STATE.

In our discussion of phase transitions we mentioned that every point in a p-T diagram corresponds to a state of the system, but that this is not necessarily the case for every point in a p-V or T-V diagram. Equation 3.15 yields a value of the pressure for all values of V and T. Hence equation 3.15 in a technical sense only represents an equation of state for those points in a T-V diagram which are equilibrium or stable states! The advantage of using an equation like 3.15 for all points is that it gives an analytic function connecting all possible regions in phase space. It has to be supplemented by equilibrium conditions. The most obvious requirements are those related to local stability. If we have p(T,V) we need $\left(\frac{\partial p}{\partial V}\right)_T \leq 0$. This inequality holds for the ideal gas law for all temperatures and volumes. All points in a T-V diagram are stable states for an ideal gas, and there are no phase transitions. This is not the case, however, for more general equations of state.

MODELS OF THE EQUATION OF STATE.

It is also possible to assume the existence of an equation of state, relating the state variables describing a system. Van der Waals analyzed such a situation. He was interested in the phase transition from a gas to a liquid and derived a modified form of the ideal gas law which is valid for both the gas and the liquid phase. The features of his model equation of state are remarkable general. The explanation for this fact is found in a microscopic derivation of his equation of state, which we will ignore at this point.

Van der Waals followed a route different from the virial approach when he investigated liquid to gas phase transitions. He postulated that for a not-so-ideal gas the equation of state should have the form

$$\left(p + a\frac{N^2}{V^2}\right)(V - Nb) = NRT \tag{3.16}$$

where a and b are two parameters. It is possible to give a physical interpretation to these parameters a and b if the Van der Waals equation of state is derived from a microscopic model. The parameter b represents the volume of a molecule. The total volume V has to be larger than the volume of all molecules tightly packed together. The internal energy of an ideal gas only depends on the temperature, and a correction term is needed for higher densities. The parameter a represents the average interaction energy between two molecules and is positive for an attractive interaction.

UNIQUE SOLUTIONS OR NOT.

The pressure as a function of volume for the van der Waals equation of state is

$$p = \frac{NRT}{V - Nb} - a\frac{N^2}{V^2} \tag{3.17}$$

Therefore, the pressure is a unique function of the volume and temperature. The volume, on the other hand, is not a unique function of the pressure and temperature, and the van der Waals equation allows for multiple solutions in certain ranges of pressure and temperature. Switching from one solution to another causes a jump in the value of the volume, exactly what we expect for a phase transition.

It is also useful to discuss the difference between the pressure in a van der Waals gas and in an ideal gas. For this difference we find:

$$p - p_{ideal} = \frac{N^2}{V^2}\left(bRT\frac{V}{V - Nb} - a\right) \tag{3.18}$$

which shows that the difference is of second order in the density. This difference is useful if we want to calculate the energy difference between a van der Waals gas and an ideal gas, for example.

UNSTABLE REGIONS.

Mechanical stability requires that compressibilities are positive, and hence $\left(\frac{\partial p}{\partial V}\right)_T < 0$. This derivative for the van der Waals equation of state is

$$\left(\frac{\partial p}{\partial V}\right)_{T,N} = -\frac{NRT}{V^2}\left(\frac{1}{(1-nb)^2} - 2a\frac{n}{RT}\right) \tag{3.19}$$

where $n = \frac{N}{V}$ is the molar density of the material in the gas or liquid. Instabilities occur when this derivative is positive. This can only happen when a is positive. In a microscopic interpretation this means that the interaction between the molecules has to be attractive. This makes sense, for if the interaction between the molecules were repulsive, they would not want to condense into a liquid. The stability condition can be rewritten in the form:

$$\frac{RT}{2a} \geq (1-nb)^2 n \tag{3.20}$$

PHASE SPACE.

Phase space for a p-V-T system is given by the octant of three dimensional $\{p, V, T\}$ space in which all three variables are positive. The van der Waals equation of state limits the possible states of the system to a two-dimensional surface in this space. The lines on this surface where the partial derivative $\left(\frac{\partial p}{\partial V}\right)_T$ is zero separates stable and unstable regions. Therefore it is of interest to find these lines by solving

$$n(1-nb)^2 = \frac{RT}{2a} \tag{3.21}$$

In order that $V > Nb$ we need $n < \frac{1}{b}$, hence we do not include the high density region in which the atoms would have to overlap in order to fit into the volume V.

CASE A=0.

There are no solutions to this equation when $a = 0$. In that case the equation of state is simply

$$p = \frac{NRT}{V - Nb} \tag{3.22}$$

which is well defined for all volumes $V > Nb$ and has a negative derivative. Hence the effect of a finite volume of the molecules in itself is not sufficient to give rise to phase transitions.

CASE B=0.
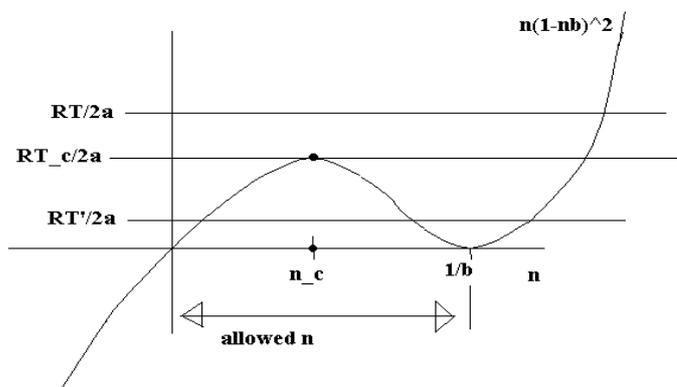
Figure 3.14: **Graphical solution of equation 3.21.**

There is only one solution to 3.21 if $b = 0$. In that case the equation of state is

$$p = n(RT - an) \qquad (3.23)$$

and stability requires $n < \frac{RT}{2a}$. This system shows a sign of a phase transition. If we start with a gas at a high temperature, and cool it down, nothing special happens as long as $T > \frac{2an}{R}$. As soon as we reach the temperature $\frac{2an}{R}$, however, the system becomes mechanically unstable, and the system collapses to a singular point with $V = 0$. The attractive interaction at low temperature is strong enough to force condensation into a liquid, but the liquid is unstable. We need the finite volume of the molecules to stabilize the liquid phase.

GENERAL CASE.

The general equation 3.21 with both a and b non-zero has either one or three solutions. In the region where the molecules do not overlap we have $n < \frac{1}{b}$. For very large values of the temperature there are no instabilities for $n < \frac{1}{b}$ and there are no phase transitions as a function of volume or density or pressure. If the temperature is very small, the solutions are approximately $n = \frac{RT}{2a}$ and $nb = 1 \pm \sqrt{\frac{RT}{2a}}$. Two solutions are in the allowed range $nb < 1$. If we increase the temperature, these two solutions will approach each other and at a certain temperature T_c they will merge together and disappear. The third solution will always be in the un-physical region $n > \frac{1}{b}$. This is represented in figure 3.14.

If the temperature T is larger than T_c, all values of n in the range $[0, \frac{1}{b}]$ correspond to mechanically stable states. On the other hand, if T is below T_c the values of N in between the two crossings correspond to mechanically unstable states, and only low and high density phases are possible.

CRITICAL TEMPERATURE.

The van der Waals equation of state shows no phase transitions for $T > T_c$ and a region of instability for $T < T_c$. Therefore T_c is identified as the critical temperature, belonging to the critical point for this liquid-gas phase transition. The derivative of the function

$$f(n) = n(1 - nb)^2 \tag{3.24}$$

is easy to find:

$$f'(n) = (1 - nb)^2 - 2nb(1 - nb) = (1 - 3nb)(1 - nb) \tag{3.25}$$

and is zero for $nb = 1$ (as expected) and $3nb = 1$. Therefore $3n_c b = 1$. This requires $b > 0$ as expected. The value of T_c follows from $\frac{RT_c}{2a} = f(n_c) = \frac{4}{27b}$. The pressure follows directly from the van der Waals equation.

LOCATION OF CRITICAL POINT.

The critical point is therefore specified by

$$RT_c = \frac{8a}{27b} \tag{3.26}$$

$$V_c = 3Nb \tag{3.27}$$

$$p_c = \frac{a}{27b^2} \tag{3.28}$$

The critical volume is indeed larger than Nb, as required. Its value, however, is close enough to the high density limit and a strict *quantitative* interpretation of the parameters a and b in terms of microscopic quantities in invalid. In such an interpretation higher order effects will certainly play a role. Therefore, it is better to consider a and b as adjustable parameters related to the interaction energy and molecular volume, and find their values from experiment. It is also clear that the equations for the critical point only make sense when a and b are positive.

pV-CURVES.

The general shape of the p-V curves is shown in figure 3.15. Note that at the critical point not only the slope of the p(V) curve is zero, but also the curvature! In addition, we have $\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{NR}{V - Nb} > 0$ and with increasing temperature the curves move always up. This means that the p-V-curves will never cross! Another interesting question pertains to the situation depicted in figure 3.16. Is it possible to have negative values of the pressure? Mechanical instability
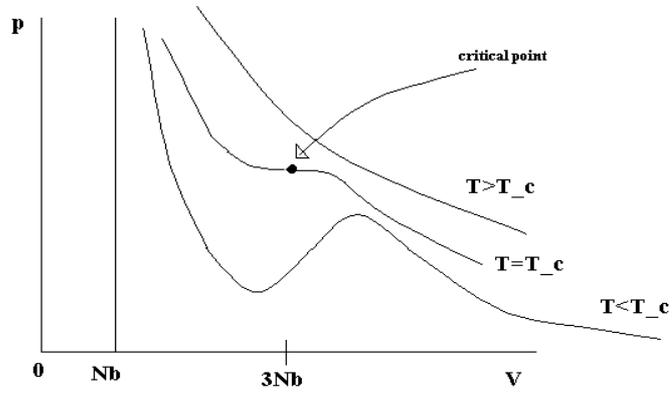
Figure 3.15: **p-V curves in the van der Waals model.**
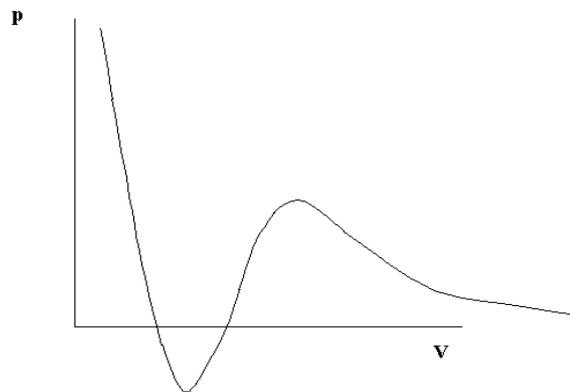
Figure 3.16: **p-V curves in the van der Waals model with negative values of the pressure.**

only requires that the slope of the p(V) curve is negative. It does not preclude a negative value of the pressure. Negative pressure means that the system gains energy by expanding. One could simulate this by connecting springs to the outside of a material, which try to stretch the material. Also, if we replace p-V by H-M there is no problem at all, negative magnetic fields are possible!

Do you expect negative pressures in real liquids?

Negative pressures occur in the van der Waals model as soon as $T < \frac{27}{32}T_c$, which means for a large range of values of the temperature. The equation $p = 0$ leads to

$$an(1 - nb) = RT \tag{3.29}$$

with solutions

$$n = \frac{1 \pm \sqrt{1 - 4RT\frac{b}{a}}}{2b} \tag{3.30}$$

which are always less than $\frac{1}{b}$ and hence always occur in the physically allowed region. The square root has to be real, though, which leads to $4RTb < a$, which gives the inequality for the temperature cited above.

FINDING THE MINIMAL ENERGY STATE.

The van der Waals equation of state for a temperature below the critical value leads to a p(V) curve of the form shown in figure 3.17. If the value of the pressure is between p_{min} and p_{max}, there are three values of the volume possible. Since the volume is a state variable, only one of these values can be correct. Obviously we have to discard the middle value of the volume, since the derivative of the p(V) curve has the wrong sign in this case. The Gibbs free energy is needed in order to decide which of the other two solutions is stable.

HOW TO CALCULATE THE ENERGY.

The difference in Gibbs free energy between the point 1 and 2 is found the change in energy along the path following the equation of state p(V) at this temperature. This is not a reversible process, since some of the intermediate states are unstable. These intermediate states are special, however, since they are mathematically well described. The equation of state is still valid for these points. At constant temperature and particle number the differential of the Gibbs free energy is $dG = V dp$ and therefore

$$G_2 - G_1 = \int_1^2 V dp = A_1 - A_2 \tag{3.31}$$
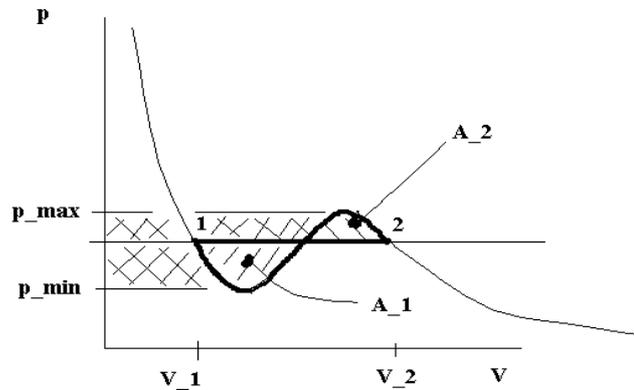
Figure 3.17: **p-V curve in the van der Waals model with areas corresponding to energies.**

where A_1 and A_2 are the indicated areas on the left and right. If $A_1 > A_2$ the Gibbs free energy of the system in state 2 is the highest and the system will be in state 1, with a low volume. The opposite is true for $A_2 > A_1$. If $A_1 = A_2$ the Gibbs free energies of both phases are equal and the liquid and gas coexist. This condition therefore determines $p_{co}(T)$.

Is this procedure allowed?

One question that might be asked is if the previous procedure is allowed. We have followed the van der Waals equation of state through unstable regions, which does not seem to be correct. Fortunately, as expected, the answer is reassuring, we can do this. At each point along the van der Waals equation of state the state of the system is an extremal state for the energy, either a maximum or a local or global minimum. If we follow the van der Waals equation of state in a reversible process, in theory we can always go back and forth and the energies calculated before correspond to the actual energy differences. Of course, in practice there would always be small fluctuations that throw us out of the unstable state when the energy is a maximum. Hence the procedure we followed is not a practical experimental procedure to measure energy differences.

Negative pressure never correspond to physical states.

The van der Waals equation of state allows for negative pressures. The equation $p = 0$ has two solutions when $T < \frac{27}{32}T_c$. The pressure at very large volumes always approaches zero inversely proportional to V. The stable state for a small, positive pressure is determined by the equality of the areas A_1 and A_2. In the limit for the pressure approaching zero, the area on the right A_2 becomes in-

finitely large. Therefore, we always have $A_2 > A_1$ in this limit, and the system will be found at the high volume state. Hence, the states with negative pressure are never stable, even though one of them is mechanically stable. Mechanical stability only involves the derivative of pressure versus volume. If a system is stable with a negative pressure, it behaves like an expanded rubber band. We need to stretch it (negative pressure) in order to keep it in that state. Stable systems with a negative pressure are possible on general thermodynamical grounds. The specific physics of the system under consideration will decide if that system can be stable under negative pressures. A liquid-gas system should not be stable under negative pressure, since cooling through forced evaporation is possible. The van der Waals equation of state is consistent with the experimental facts for a liquid-gas system and does not allow for stable states with a negative pressure. All in all we conclude that the van der Waals equation of state is a good model for a liquid to gas phase transition, ending in a critical point.

3.6   Spinodal decomposition.

Names of separation lines.

The van der Waals equation of state determines the temperature as a function of pressure and volume for every point (state) in the p-V plane. As we have seen, however, not all states are stable. The region in the p-V plane where $\left(\frac{\partial p}{\partial V} \right)_{T,N} > 0$ corresponds to mechanically unstable states. The line which separates this region from the region of mechanically stable (but thermodynamically meta-stable) states is called the <u>spinodal</u> and is determined by $\left(\frac{\partial p}{\partial V} \right)_{T,N} (p, V, N) = 0$. One has to keep in mind that N is fixed. The line separating the thermodynamically stable and meta-stable states is called a <u>binodal</u> and is determined by the condition that the Gibbs free energy be the same in both phases.

Meta-stable regions.

What happens when we prepare a system in the mechanically unstable region? This could be done, for example, by cooling a system with volume V_c rapidly to a temperature below T_c. Assume that the pressure for this un-physical system is p_0, and that the system is kept at a constant temperature T_0. At first, the system will be homogeneous. Since it is mechanically unstable, any small fluctuation in the density will be amplified. A region which momentarily has a density which is too high, will increase its density following the van der Waals curve until it reaches the spinodal, where it becomes mechanically stable. A low density region will follow the van der Waals curve in the opposite direction.
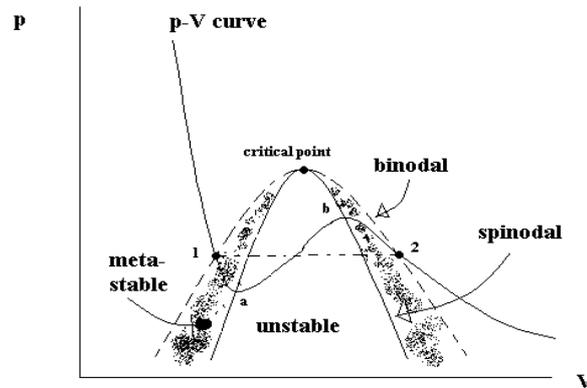
Figure 3.18: **Unstable and meta-stable regions in the van der Waals p-V diagram.**

The system will separate in small areas of high density, with total volume V_a, and small areas with low density with volume V_b. This regions are all mixed together. The total volume has to be constant, and hence $V_{total} = V_a + V_b$ where V_{total} is the initial volume. Also we have $N = N_a + N_b$. These two relations together determine how much material will go into each phase.

SPINODAL DECOMPOSITION.

The process described in the previous section is an important one and is called spinodal decomposition. The end state is mechanically stable. It is thermodynamically unstable, though, since $p_a < p_b$. Hence the process will continue by a further expansion of the low density regions and a further contraction of the high density regions until the pressure in both regions is equal again (and equal to p_0). During this process we again follow a van der Waals curve. But now *time scales* become important.

SPINODAL DECOMPOSITION IN A LIQUID-GAS SYSTEM.

If the spinodal decomposition occurred in a gas-liquid mixture, the road to thermal equilibrium is without obstacles and the final system will be a mixture of gas and liquid at the same pressure p_0 and temperature T_0 (corresponding to points 1 and 2 in figure 3.18). The amount of each material is determined by the original volume of the gas. In free space, this is exactly what happens. Clouds and fog are such mixtures of gas and liquid. One way to do an experiment along these lines is to take a liquid in a cylinder with a piston and suddenly pull the piston out.

COMPLICATING FACTORS.

In many experiments gravity plays a role and will try to collect all the liquid in the bottom of the container. Surface tension is another factor, and has to be taken into account to find the distribution of the sizes of the liquid droplets in a fog. Note that it is possible for a system to be in the meta-stable region. Water can be under-cooled well below 0 C. Any small perturbation (like an abrupt movement of the container) will cause it to freeze, however, demonstrating the meta-stability.

EXAMPLE IN BINARY PHASE DIAGRAM.

In a solid compound $A_x B_{1-x}$ the composition x is a state variable and a spinodal curve might show up in the T-x plane. Certain compositions are mechanically unstable in that case, and if we quench a liquid of that combination to a low temperature, the quenched solid is mechanically unstable. It will phase separate following a spinodal decomposition and become a mixture of grains of the compound with low x and high x. The intensive state variable corresponding to the concentration x is the chemical potential. Therefore, we have created differences in chemical potential between the grains, and this will force material to move, so we can follow the equivalent of a p-V curve to arrive at the stable states for this temperature. In order to do so, however, material needs to diffuse in a solid, which is a very slow process. When the system has become mechanically stable, it might try to find other ways to rearrange and become thermodynamically stable. In a solid, however, the grains of each material cannot be deformed randomly and the elastic properties of the material will determine how close the system is able to approach thermodynamical equilibrium. In most cases, large internal stresses will persist, which has lots of implications for the strength of the material.

What are the consequences for the measurement of phase diagrams?

If we cool a binary alloy, with a concentration corresponding to a stable state, from the liquid, do we get a homogeneous solid?

AN ENERGY VIEW OF THE DECOMPOSITION

If we follow the Helmholtz free energy as a function of volume at a given temperature below the critical temperature, we find a behavior as sketched in
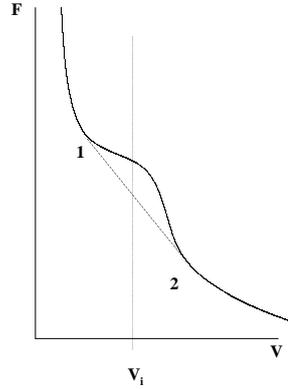
Figure 3.19: **Energy versus volume showing that decomposition lowers the energy.**

figure 3.19. The slope of the energy curve at each point gives us the pressure at that state (with a minus sign). The Helmholtz energy is calculated by the following integration along the equation of state:

$$F(V, T, N) = F_0(T, N) - \int_{V_0}^{V} p\,dV \qquad (3.32)$$

where the integration variable is now V (because we switched to the Helmholtz free energy).

Suppose we are at a volume V_i in between points 1 and 2. In that case the Helmholtz free energy obtained by following the van der Waals equation of state is larger that the value obtained by drawing a straight line between 1 and 2. What does the latter mean? It corresponds to creating a mixture of materials corresponding to the states at points 1 and 2. The equation of the straight line connecting 1 and 2 is

$$F_s(V) = \frac{1}{V_2 - V_1} \left((V_2 - V)F_1 + (V - V_1)F_2 \right) \qquad (3.33)$$

which corresponds to a fraction $x_1 = \frac{V_2 - V}{V_2 - V_1}$ of material in state 1, and $x_2 = \frac{V - V_1}{V_2 - V_1}$ in state 2. It is easy to check that this indeed adds up to the correct volume, $x_1 V_1 + x_2 V_2 = V$. Therefore, in any point between 1 and 2 we can lower the energy of the material by phase separation.

How do we find the location of points 1 and 2? They need to have the same slope, hence

$$\left(\frac{\partial F}{\partial V} \right)_{T,N} (V_1) = \left(\frac{\partial F}{\partial V} \right)_{T,N} (V_2) = -p_{coex} \qquad (3.34)$$

and this slope should be the slope of the connecting line:

$$\left(\frac{\partial F}{\partial V}\right)_{T,N}(V_1) = \frac{F_2 - F_1}{V_2 - V_1} \tag{3.35}$$

which leads to

$$p_{coex}(V_2 - V_1) = -(F_2 - F_1) = \int_1^2 p dV \tag{3.36}$$

which is an alternative formulation of the statement that the areas are equal. This approach is due to Maxwell, and the graphical approach in figure 3.19 is called the Maxwell construction.

3.7   Generalizations of the van der Waals equation.

The van der Waals equation takes a very simple form when expressed in values of the state variables relative to the critical values. Define

$$\mathcal{P} = \frac{p}{p_c}, \mathcal{V} = \frac{V}{V_c}, \mathcal{T} = \frac{T}{T_c} \tag{3.37}$$

The van der Waals equation of state in these variables is

$$\left(\mathcal{P} + \frac{3}{\mathcal{V}^2}\right)\left(\mathcal{V} - \frac{1}{3}\right) = \frac{8\mathcal{T}}{3} \tag{3.38}$$

which is independent of p_c, V_c, and T_c! In relative state variables the van der Waals equation does not contain any information about the specific system and in these units the binodal coexistence curve $\mathcal{T}(\mathcal{V})$ should be the same for all materials. This has indeed been observed for a number of different substances like inert gases. The binodal curves for these substances in relative units are almost identical. This common binodal curve differs somewhat from that predicted by the van der Waals equation, however, and corrections to the higher order virial coefficients are needed. Nevertheless, ignoring these relatively small differences, it is amazing how well the van der Waals equation of state describes a liquid to gas phase transition, and predicts the universality of the spinodal curve. In order to understand the reasons for this success, one has to look at the microscopic foundation of the van der Waals equation. Also, the notion that the equations of state in scaled units are the same for similar materials introduces for the first time the idea of universality. If the same physics is at work in different materials, it is possible to scale experimental results from one to the other.

MIXTURES.

The van der Waals equation can also be extended to mixtures. In this case it looses many of its simple characteristics. For a gas mixture of M species, the

excluded volumes are b_i and the average interactions are a_{ij}. The number of atoms of type i is N_i. The simplest generalization of the van der Waals equation for this case is

$$\left(p + \frac{1}{V^2} \sum_{i<j} a_{ij} N_i N_j \right) \left(V - \sum_{i=1}^{M} N_i b_i \right) = NRT \qquad (3.39)$$

If we define the relative concentrations like $x_i = \frac{N_i}{N}$, it is possible to rewrite this equation in a form similar to the original van der Waals equation

$$\left(p + a(x_i) \frac{N^2}{V^2} \right) (V - Nb(x_i)) = NRT \qquad (3.40)$$

where the functions a and b only depend on the composition. As is turns out, this generalization is not correct from a microscopic point of view. The change in the first factor can be explained in terms of particle-particle interactions. Although the modification of the second factor intuitively seems correct, a statistical mechanical approach yields a more complicated expression.

3.8 Extra equations.

1. *What is the most important phase transition?*

2. *Can we have a solid to gas transition?*

3. *Why is G continuous?*

4. *Why does V drop with p?*

5. *Can V be continuous?*

6. *Should V drop with T?*

7. *Consider a container with water and vapor. Increase T. What is formed?*

8. *What happens at the critical point in an experiment?*

9. *Suppose we have two phases coexisting with $p_1 = p2$, $T_1 = T_2$, but $\mu_1 \neq \mu_2$. What happens?*

10. *Why is it easiest to discuss phase boundaries using the Gibbs free energy?*

11. *What can you tell about the slope of the coexistence curve?*

12. *Could ice 1 and ice 2 meet by accident at the triple point?*

13. *Apply Clausius-Clapeyron to a superconducting phase transition in B field.*

14. *What are the consequences for the slope of p_{co} at the water-ice boundary?*

15. *How do you measure phase diagrams?*

16. *Construct phase diagram with a compound forming at low T.*

17. *What determines the curvature of the lines in a binary phase diagram?*

18. *Do perfect compounds exist at low temperature?*

19. *What does universality of the van der Waals equation mean?*

20. *Discuss the meaning of the sign of the second virial coefficient.*

21. *Show that $\eta_{JT} = -\frac{N}{C_p} B_2$ for constant B_2*

22. *Give an example of a system which has a negative pressure.*

23. *How did we get the unstable region in the forbidden region?*

24. *Why can we measure the spinodal curve?*

25. *Can the curves $p(V, T_1)$ and $p(V, T_2)$ cross?*

26. *Explain equal areas in terms of work done.*

27. *Why do we need the Gibbs free energy to decide in the vdW equation, but use the Helmholz free energy in the Maxwell construction?*

3.9   Problems for chapter 3

PROBLEM 1.

The equation of state for some material is given by the first two terms of a virial expansion,

$$\frac{p}{RT} = \frac{N}{V}\left(1 + B_2(T)\frac{N}{V}\right) \tag{3.41}$$

The second virial coefficient $B_2(T)$ has a very simple form, $B_2(T) = \frac{R}{p_0}(T - T_0)$.

(a) Make a picture of the isotherms in a p-V diagram.

(b) Sketch the region of points (p,V) which correspond to unstable states.

(c) Sketch the region of unstable states in the V-T diagram.

(d) Are there any meta-stable states?

PROBLEM 2.

The van der Waals equation of state is not the only form proposed to study phase transitions. Dietrici investigated the following expression:

$$p(V - Nb) = NRTe^{-\frac{aN}{RTV}} \tag{3.42}$$

(a) Show that in the limit $V \gg N$ this equation of state becomes equivalent to the ideal gas law.

(b) Calculate V_c, T_c, and p_c for this equation of state.

(c) Sketch the isotherms in a p-V plane for $T > T_c$, $T = T_c$, and $T < T_c$.

PROBLEM 3.

Drops of a liquid are in equilibrium with a gas of the same material. This experiment is done in an environment where there is no gravity, so the drops float freely in the vapor. The drops are spherical because of surface tension. For a given drop, the change in energy dU is given by

$$dU = TdS - pdV + \mu dN + \sigma dA \tag{3.43}$$

where A is the surface area of the drop.

(a) Show that for *spherical* drops this relation can be written in the form

$$dU = TdS - p_{eff}dV + \mu dN \tag{3.44}$$

(b) How is the pressure inside this spherical drop related to the pressure in the vapor?

The chemical potential of the liquid is $\mu_l(p, T)$ and for the gas $\mu_g(p, T)$. Assume that both gas and liquid have the same temperature T.

(c) What is the equilibrium condition which determines that in equilibrium there is no net flow of particles between the liquid and the vapor?

(d) Generalize the Clausius-Clapeyron relation for a system of vapor and spherical droplets, including surface tension.

(e) Show that the coexistence pressure of the vapor at a given temperature increases when the average radius of the droplets decreases.

PROBLEM 4.

A closed container contains water and helium gas. Assume that helium does not dissolve in water.

(a) Show that at a given pressure there is at most one temperature at which water, ice, and water vapor coexist.

(b) The triple point for water is p_t, T_t. Calculate the change in these values as a function of the Helium pressure. Assume that the chemical potential of water is independent of pressure

PROBLEM 5.

Show that the latent heat per mole of the liquid to vapor phase transition using the van der Waals equation of state is given by

$$l_{1 \to 2}(T) = RT \ln \left(\frac{V_2 - Nb}{V_1 - Nb} \right) \qquad (3.45)$$

PROBLEM 6.

(A) Calculate the difference in Helmholtz free energy between a van der Waals gas and an ideal gas using $F = -pdV$ at constant temperature and number of moles of material. Assume that this difference is zero in the limit $V \to \infty$.

(B) Calculate the difference in entropy between a van der Waals gas and an ideal gas at constant temperature and number of moles of material. Assume that this difference is zero in the limit $V \to \infty$.

(C) Show that the constant "a" in the van der Waals equation of state leads to a term $-a\frac{N^2}{V^2}$ in the internal energy of a van der Waals gas. Interpret this term in a molecular picture.

PROBLEM 7.

(A) For values of the temperature below the critical temperature find an upper and a lower limit for the transition pressure in a van der Waals gas.

(B) For values of the temperature below the critical temperature and values of the pressure in between these two limits, the van der Waals equation of state has two mechanically stable solutions with volumes V_l and V_h. Calculate the difference in Gibbs free energy between these two states.

(C) Outline a procedure for calculating the coexistence curve $p_{co}(T)$ numerically.

PROBLEM 8.

The boiling point of Hg is 357C at 1 atm. and 399C at 2 atm. The density of liquid mercury is 13.6 g/cm^3. The heat of vaporization is 270 J/g. Calculate the order of magnitude of the volume of 200g Hg vapor at 357C and 1 atm. Note, 1 atm. is about $10^5 N/m^2$, 0C=273K, and G=U-TS+pV.

PROBLEM 9.

For a certain material the gas and liquid phase coexist even at 0K. Show that the third law implies that $\frac{dp_{co}}{dT} = 0$ at T=0.

PROBLEM 10.

A closed container of volume V_0 contains N_0 moles of material, partly liquid, partly gas, in equilibrium. The energy is constant, the container is thermally isolated. The gas is ideal, with $pV = NRT$. The Gibbs free energy of the liquid is $G_l(p, T, N) = N\mu_l(p, T)$. The unknown variables are (1) the number of moles N_g in the gas phase, (2) the number of moles N_l in the liquid phase, (3) the volume V_g of the gas phase, and (4) the volume V_l of the liquid phase.

(A) Why are the pressure and temperature in the gas phase the same as in the liquid phase?

(B) Specify four equations which we need to solve to find the four unknown quantities, given that the pressure in the container is p and the temperature is T.

(C) Solve this system of equations for N_l

(D) Is there a solution for all values of p and T?

PROBLEM 11.

In the vicinity of the triple point of a material the vapor pressure of the liquid is given by $\log(\frac{p}{p_0}) = 10 - \frac{20T_0}{T}$. The vapor pressure of the solid is given by $\log(\frac{p}{p_0}) = 15 - \frac{25T_0}{T}$.

(A) What are the temperature and the pressure of the triple point in terms of T_0 and p_0?

(B) Using the Clausius-Clapeyron equation, show that $\frac{d\log(p_{co})}{dT} = \frac{l}{p_{co}T\Delta v}$.

(C) Is the volume per mole of the gas larger or smaller than that of the liquid, assuming that T_0 and p_0 are both positive?

(D) Assume that the values of the latent heat are independent of temperature near the triple point, and that the molar volume of the gas is much larger than the molar volume of the liquid and of the solid. Calculate the ratios $l_{SL} : l_{LG} : l_{SG}$, where S,L, and G stand for solid, liquid, and gas.

PROBLEM 12.

Grüneisen parameter.

In many solids we can approximate the entropy by $S = Nf(T/T_D)$ where the Debye temperature T_D is a function of the molar volume only, $T_D = g(\frac{V}{N})$. The Grüneisen parameter γ_g is defined by

$$\gamma_g = -\frac{V}{NT_D}\frac{dT_D}{d\frac{V}{N}}$$

Show that

$$\gamma_g = \frac{V\alpha}{C_V \kappa_T}$$

For many solids the Grüneisen parameter is almost constant. If we assume that it is a constant, show that we have the equation of state

$$PV = \gamma_g U + Nh(\frac{V}{N})$$

This is the Mie-Grüneisen equation of state.

PROBLEM 13.

Murnaghan equation.

The isothermal bulk modulus B_T is given by $B_T = -V\left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{\kappa_T}$. The bulk modulus can often be approximated by $B_T(p,T) = B_T(0,T) + \beta_T p$ where β_T is independent of pressure.
Show that this leads to the equation of state

$$p(V,T) = \frac{B_T(0,T)}{\beta_T}\left(\left[\frac{V_0}{V}\right]_T^\beta - 1\right)$$

where V_0 is the volume at $p = 0$ and temperature T.

PROBLEM 14.

Derive the virial coefficients $B_j(T)$ for the Van der Waals equation of state. Comment on the sign of the second virial coefficient.

PROBLEM 15.

The Gibbs free energy of pure materials A and B is given by $N_A \mu_A(p, T)$ and $N_B \mu_B(p, T)$. The entropy of mixing for materials A and B is $-N_A R \log(\frac{N_A}{N_A+N_B}) - N_B R \log(\frac{N_B}{N_A+N_B})$, while the interaction energy between A and B is given by $A(T, p)\frac{N_A N_B}{N_A+N_B}$. Show that a system where we mix N_A moles of A and N_B moles of B is stable for $2RT > A$ and that there are forbidden regions when $2RT < A$.

Chapter 4

Landau-Ginzburg theory.

4.1 Introduction.

PHASE TRANSITION IN EQUILIBRIUM THERMODYNAMICS.

Equilibrium thermodynamics as presented in the previous chapters gives us state functions and free energies. In particular, we should be able to find the Gibbs free energy G(p,T,N). In Chapter 3 we used these ideas to describe phase transitions. Suppose a system can exist in two different phases, 1 and 2, and we have a model for the Gibbs free energy in each phase. For each value of the temperature and pressure we can therefore determine the Gibbs free energy of each phase, and by comparing the values we can determine which phase is stable and which is meta-stable. Sometimes we do not have the explicit forms of the free energies, but have a model equation of state (like the van der Waals equation of state) which allows us to relate the free energies of the two phases to each other. Since only the difference in free energy is important, this approach is equivalent to the one sketched first.

WHAT HAPPENS AT THE TRANSITION?

The approach outlined above is very useful, since it gives us equations like the Clausius-Clapeyron equation which tell us how phase boundaries change. This approach is an either/or approach, however. It allows us to determine which phase is stable, but it does not say anything about the transition. For example, the heat capacity as a function of temperature in the van der Waals model looks like figure 4.1, while experimentally it looks much more like figure 4.2. There is a critical region in which the heat capacity is very large (and perhaps even divergent). The width of this region could be 10K or 1mK, depending on the material.
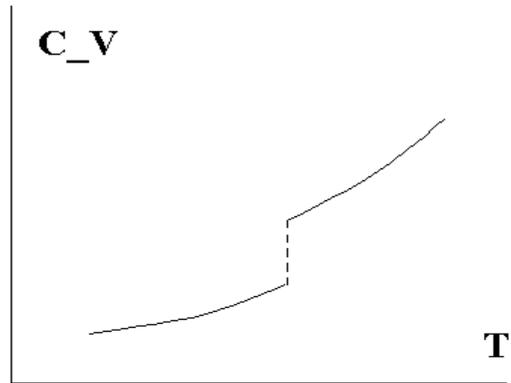
Figure 4.1: **Heat capacity across the phase transition in the van der Waals model.**
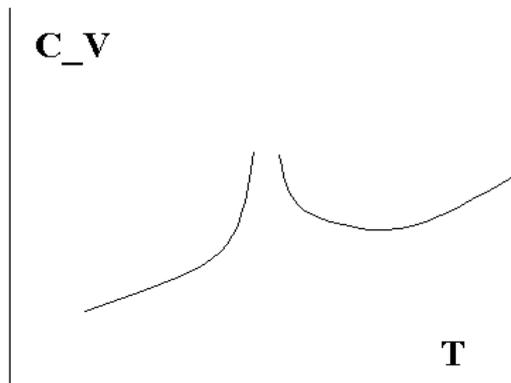
Figure 4.2: **Heat capacity across the phase transition in an experiment.**

The next question is what is missing from our simple equilibrium thermodynamics model? Anyone who has seen water boil knows the answer. There are fluctuations in the system. Even below the boiling point vapor bubbles appear in water. These instabilities live only a short time, but when we get closer to the boiling point, the vapor bubbles become larger and live longer. To describe what is happening is very difficult, and we need a non-equilibrium theory. It is very important in practical applications, though. Any preparation technique of a material that involves a phase transition has to deal with this question, and understanding and being able to change the mechanism could be worth millions of dollars for industry. In this chapter we describe a theory developed by Landau and Ginzburg, which is a first approach at incorporating the effects of fluctuations.

4.2 Order parameters.

How do we bring order or organization into chaos?

HOW DO WE DESCRIBE A PHASE TRANSITION?

Phase transitions are observed by doing measurements. The question is, what do we measure? The phase transition from water to ice is easy to observe experimentally. The properties of water and ice are very different and we rely on the fact that these properties have a range of values to distinguish between ice and water. Since snow is also frozen water, but different from ice, we also know that not all properties of ice are characteristic for frozen water. We need to single out one or more parameters which will really tell us which phase we are dealing with. In a solid the relative positions of the molecules are fixed (within small vibrations) but in a liquid the molecules are able to move freely. In a liquid the motion of the molecules is locally correlated, and the local neighborhood of a molecule in a liquid is similar to that of a molecule in a solid. There is no long range order, though. In a gas, even the local correlation has disappeared, and the molecules are almost independent.

REQUIREMENTS FOR CHARACTERIZING PARAMETER.

If we want to describe a phase transition in mathematical terms, we need to find a parameter which uniquely defines which phase we are in. Therefore, this parameter has to be a state variable. In a gas to liquid transition we used the

volume to distinguish between the low and high density phases, but this choice
has some problems. If we use a state variable to distinguish between different
phases of a system, it has to be measurable. Hence, it must be possible to use
this state variable to do work. But we also require that a measurement of this
state variable does not change the phase of the system, hence in principle is
should be measured with a corresponding field which approaches zero. In that
case the state variable we use to describe the phase of the system is considered
an internal parameter. It also has to be an extensive parameter. The volume in
a gas to liquid transformation could play this role, but the ideal gas law in the
limit $p \to 0$ becomes singular. To describe a gas one needs a non-zero pressure,
and the work done by changing the volume becomes an essential part of the
physics of a gas to liquid phase transition.

ORDER PARAMETER.

A state variable which is used to describe the phase of a system is called
an order parameter. The difference in molar volume between the phase under
consideration and the gas phase is an example of an order parameter. This order
parameter is zero in the gas phase, but non-zero in the liquid phase. Another
standard example is the magnetic moment $\vec{M}$ of a solid. We often use the molar
density $\frac{\vec{M}}{N}$ in stead. This order parameter is zero in the non-magnetic phase,
but non-zero in the ferro-magnetic phase. There is always a generalized force
associated with the order parameter, the corresponding intensive state variable.
For the liquid to gas transition this is the pressure p and for the magnetic system
it is the magnetic field $\vec{H}$. This generalized force is what we need to apply in
order to be able to measure the value of the order parameter.

MEASURING THE ORDER PARAMETER.

The external parameters used to determine the state a solid are often the
temperature T and the pressure p. For the following discussion, let us assume
that we work at atmospheric pressure, which is essentially zero for a solid. The
appropriate free energy for a system at constant temperature is the Helmholtz
energy F, which in our case only depends on the state variables T (determined
by the outside world) and $\vec{M}$ (used to determine the state of the system). The
Helmholtz free energy of the thermodynamic equilibrium state is found by min-
imizing F as a function of $\vec{M}$. This is consistent with the following observation.
In the process of measuring the order parameter we need to consider it as an
external state variable. In our case the measurement consists of applying a field
$\vec{H}$ and the appropriate free energy in that case is the Gibbs like free energy

$$\mathcal{G}(T, \vec{H}) = U - TS - \vec{M} \cdot \vec{H} \qquad (4.1)$$

Measuring the work done on the sample at constant temperature as a function
of field gives this energy, and the partial derivative with respect to $\vec{H}$ in the
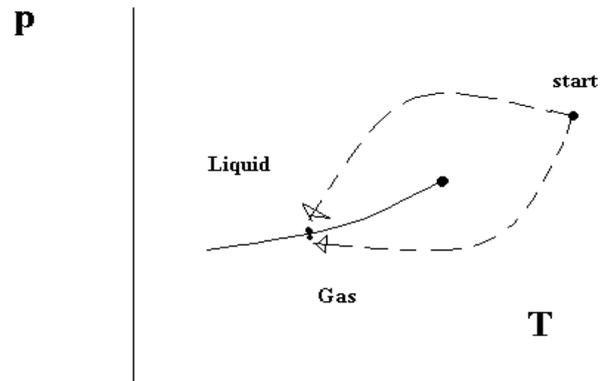
Figure 4.3: **Continuity of phase transition around critical point in p-T plane.**

limit $\vec{H} \to \vec{0}$ gives us $\vec{M}$ as required. When we consider the magnetic moment as an external parameter, it is related to the external field via

$$\left(\frac{\partial F}{\partial \vec{M}} \right)_T = \vec{H} \qquad (4.2)$$

and this partial derivative is indeed zero in the limit $\vec{H} \to \vec{0}$. In conclusion, the free energy used to describe the system and the free energy used to describe the measurement of the order parameter differ by a simple Legendre transformation.

PHASE TRANSITIONS WITH CRITICAL POINT.

In the phase diagram for a PVT-system we find two different types of behavior. The transition from solid to gas or liquid is described by a coexistence curve which probably extends to infinity. There is no critical point. The liquid to gas coexistence curve, on the other hand, ends in a critical point. If we start at a state of the system at a high temperature, and cool the system at low pressure, we will end up in the gas phase. The same procedure at high pressure gives a liquid. Hence from any given initial state one can reach a state just above or below the coexistence curve in a continuous manner. This is shown in figure 4.3. One way of defining the order of a phase transition is using this continuity. A phase transition is called second order if it is possible to find a continuous path around a critical point from one phase to the other, and it is called first order if this is not the case. Note, however, that other definitions of the order of a phase transition are in use, too.

BRANCH CUTS.
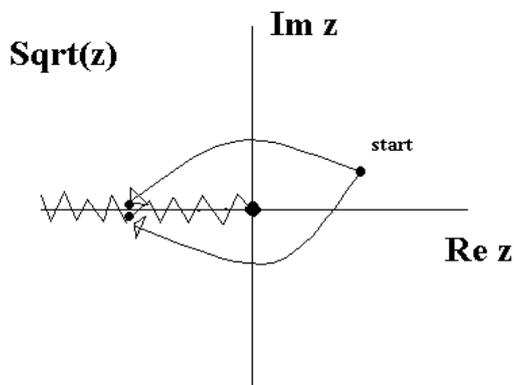
Figure 4.4: **Continuity of phase around singular point.**

The coexistence curve plays a role which is very similar to that of a branch cut in a complex function. The function $\sqrt{z}$, for example, shows a similar picture which a line of discontinuities, see figure 4.4. From any initial value of z it is possible to go to a point just below or just above the branch cut in a continuous manner. The branch cut represents a line of discontinuities. The critical point in the p-T diagram is comparable to the essential singularity which ends a branch cut. Just like $\sqrt{z}$ cannot be described by a power series at $z = 0$, the function V(p,T) has an essential singularity at p_c, T_c. This approach has been generalized. All we need to know is the exact behavior of V(p,T) *at the singularity* in order to predict what is happening near this point. This is very much like the complex analysis of a singular complex function. A magnetic phase transition is characterized in the same way by a real singular point T_c, H_c. If the system is symmetric for the change $M \Leftrightarrow -M$, it follows that $H_c = 0$ and the singular behavior in the H-T plane is like in figure 4.5.

What conclusions can you draw from the similarity between the mathematical forms of the free energy and a branch cut?

SYMMETRY IN SYSTEM.

When the external field coupling to the order parameter is zero, one often expects the free energy to be symmetric as a function of the order parameter. This is not true in general, since a vanishing external field only requires that the first order derivative is zero. But if we consider this simple symmetric case the free energy of the system without field is the same for a given value of the order parameter and for the opposite value. The most symmetric situation therefore
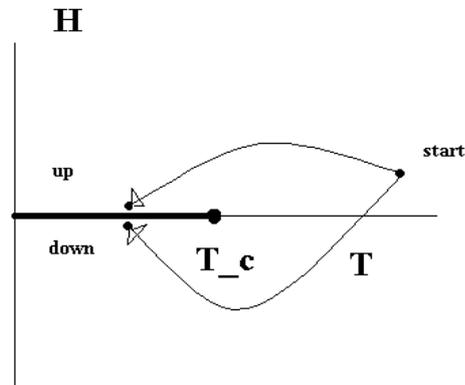
Figure 4.5: **Continuity of phase transition around critical point in H-T plane.**

will have a value of zero for the order parameter. This does often, but not necessarily, correspond to the state of the system at high temperatures. For example, $\vec{M} = \vec{0}$ at high temperatures. There is no preferred direction of the magnetization. When we apply a magnetic field we will have in general that $\vec{M} \| \vec{H}$.

NO SINGULARITIES IN FINITE SYSTEM.

If the equilibrium state of the system has a non-zero value of the order parameter, there are at least two states for the system with the same energy, corresponding to a certain value of the order parameter and to the opposite value. Therefore in that case the ground state is degenerate. Although in principle the state of the system can fluctuate between these degenerate ground states, the time involved is in practice infinitely long since macroscopic variables are involved. Quantum mechanical tunnelling is highly improbable in that case. But we also need to remember that we have to take the thermodynamic limit $N \to \infty$. In that case the tunnelling time becomes infinitely long, and the system is found in one state only. There is a mathematical statement that says that for a finite system there are no singularities in state functions! Hence sharp transitions and critical points only occur in infinite systems!

What do phase transitions look like in finite systems?

When is a finite system infinite for all practical purposes?

BROKEN SYMMETRY.

At the coexistence curve the system chooses one of the possible ground states, and breaks the symmetry between the possible values of the order parameter by choosing a particular one. In a scenario like we sketched here a phase transition is related to spontaneously broken symmetry in a degenerate ground state. Of course, the external field used to measure the order parameter, will always break the symmetry. In that case the broken symmetry is forced by external constraints.

SUPERCOOLING AND SUPERHEATING.

If we follow a complex function like $\sqrt{z}$ in a continuous manner through a branch cut, we end up on the wrong Riemann sheet. In the case of $\sqrt{z}$ this simply means that we end up with the wrong sign, since there are only two Riemann sheets. If we go continuously through a coexistence curve, we end up in a meta-stable state. Water vapor, for example, can be super-saturated. Introducing so-called seeds will then allow droplets of liquid to form around these seeds, and will force the transition to the stable liquid state.

Could a free energy have more than two Riemann sheets, and if so, can they be observed?

ESSENTIAL SINGULARITY.

A branch cut of a complex function end in an essential singularity, like the point z=0 for the function $\sqrt{z}$. Second order phase transitions end in an essential singularity at the critical point. Mathematically, the idea of a critical point and an essential singularity are closely related.

MODEL SYSTEMS.

The gas to liquid phase transition is not easy to describe. The problem is that a gas has a non-zero volume, and that a non-zero pressure exists, needed for thermal equilibrium. The driving force is non-zero! Therefore we need to consider quantities like the difference in volume and the difference in pressure. A symmetric magnetic phase transition is easier to describe. In one phase we have M=0, which occurs at H=0, and in the other phase we have a finite value of the magnitude M. Choosing M as the order parameter is therefore equivalent to choosing **half** the difference between the volumes in the liquid to gas system as the order parameter. Since magnetic systems are easier to model, we will use these systems as examples in the rest of this chapter. A model of a liquid to gas

transition, however, can be done in a similar manner, and only the mathematical description becomes more elaborate.

4.3 Landau theory of phase transitions.

ENERGY IS THE BASIC QUANTITY.

Landau devised a very simple method to describe phase transitions. It is similar in spirit to the approach of van der Waals, but on a more fundamental level. Landau recognized that the free energy is the important state function to parameterize, since all other relations follow from a knowledge of the free energy. The route van der Waals followed is more empirical. The van der Waals equation of state works very well for a liquid-gas transition, but is hard to generalize to other phase transitions. Landau suggested to parameterize the free energy as a function of the order parameter.

MAGNETIC SYSTEMS ARE GOOD WORKING EXAMPLE.

We will use a magnetic system as an example. We will assume that the system has rotational symmetry, and that the free energy does not depend on the *direction* of the magnetization $\vec{M}$, but only on its value M, apart from the obvious minus sign that reflects up or down. In this discussion we therefore allow M to be negative, which is necessary in order to show the degeneracy of the ground state. We assume that we use the temperature T as an independent variable, and that the volume V and the amount of material N are constant. Therefore, we need to work with the Helmholtz free energy.

The applied magnetic field follows from $\left(\frac{\partial F}{\partial M}\right)_{T,V,N} = H$ and since we plan to discuss the stable state at zero applied field, this partial derivative is zero. We now switch our point of view, and consider M to be an internal parameter. The condition mentioned before is now consistent with the fact that the Helmholtz free is a minimum as a function of the internal parameters. Since V and N are constant, we will drop these variables from the discussion, unless explicitly needed.

MODEL HELMHOLTZ ENERGY.

Because of the symmetry we imposed we have $F(T, M) = F(T, -M)$ and an expansion of the free energy F only contains even powers of M. Because of this symmetry the state with M=0 always corresponds to zero applied external field. This state is therefore an extremum, but could be a maximum. If the minimum of the free energy occurs at a non-zero value of M, there will always be two minima, +M and -M. These are states with a spontaneous magnetization and give rise to the broken symmetry discussed before.

Landau studied the following form for the free energy:

$$f(T, m) = a(T) + \frac{1}{2}b(T)m^2 + \frac{1}{4}c(T)m^4 + \frac{1}{6}d(T)m^6 + \cdots \qquad (4.3)$$

This specifies the Helmholtz free energy per unit volume, $f = \frac{F}{V}$, as a function of the average magnetization density, $m = \frac{M}{V}$. The advantage of a formulation in terms of energy and magnetization densities is that it does not depend on the size of the system. The coefficients a(T), etc. are intensive quantities. They take the form as expected in the thermodynamic limit, and are not dependent on N and V (but could depend on the density $n = \frac{N}{V}$ or equivalently on the pressure p, which dependence we will ignore here for simplicity).

VALIDITY OF THE EXPANSION.

One problem comes to mind at once. Landau assumed that the order parameter is the same for the whole system. When the system changes phase, however, there is a coexistence of both phases and the order parameter depends strongly on position and time. This short-coming of the theory is not essential, and the improved theory of Ginzburg and Landau takes fluctuations into account, as we will discuss later. But, as we discussed before, at T_c there is an essential singularity, and a power series is not appropriate, because it *fails to converge*! Hence **Landau's theory in not able to describe exactly what is happening for the phase transition at a critical point**!

VALUE OF THE THEORY.

Landau's theory is very versatile for classifying all kinds of phase transitions by comparing the states at both sides of the transition. Keep in mind that Landau's theory was developed in 1936, before many models were solved analytically. By assuming very general functional forms for the coefficients a(T),b(T),$\cdots$, only a few basic types of phase transitions appear. Experimentalists use Landau theory very often to interpret their data, because it is a good macroscopic, first approach. It is therefore a good meeting ground for theory and experiment. Complex theoretical calculations should try to derive the functional forms of the coefficients in Landau's expansion, while experimentalists can measure them. This gives an excellent framework to discuss agreements and conflicts.

The use of this classification of phase transitions has been very helpful in understanding phase transitions, and is done later more rigorously in renormalization group theory. It also is another hint at universality, phase transitions with a similar analytical form of the coefficients behave essentially in the same way. This forms a basis for scaling theory, which is discussed in the next chapter.

4.4 Case one: a second order phase transition.

One of the basic phase transitions is found when we assume that $b(T) = b_0(T - T_c)$ with $b_0 > 0$, and $c(T) = c > 0$, $d(T) = d > 0$, with all higher order coefficients vanishing. Hence we study what happens when the first coefficient changes sign. The last coefficient, d, has to be positive or else the minimum free energy would occur at infinite magnetization. The partial derivatives are:

$$\left(\frac{\partial f}{\partial m}\right)_T = b_0(T - T_c)m + cm^3 + dm^5 \tag{4.4}$$

$$\left(\frac{\partial^2 f}{\partial m^2}\right)_T = b_0(T - T_c) + 3cm^2 + 5dm^4 \tag{4.5}$$

The slope is zero if either

$$m = 0 \tag{4.6}$$

$$b_0(T - T_c) + cm^2 + dm^4 = 0 \tag{4.7}$$

In the first case this only corresponds to a minimum in the free energy if $T > T_c$, otherwise the curvature of the free energy 4.5 would be negative. If a solution for m exists in the second case, it always corresponds to a local minimum since the curvature 4.5 in that case is $2cm^2 + 4dm^4$, which is always positive. In order to see if this state is the equilibrium state we have to compare the free energies. We have

$$f(T, m) - f(T, 0) = \frac{1}{2}b_0(T - T_c)m^2 + \frac{1}{4}cm^4 + \frac{1}{6}dm^6 =$$

$$\frac{1}{2}\langle b_0(T - T_c) + cm^2 + dm^4 \rangle m^2 - \frac{1}{4}cm^4 - \frac{1}{3}dm^6 \tag{4.8}$$

and this is always negative in the second case. Hence if 4.7 has a solution, this solution corresponds to the equilibrium state.

GENERAL NON-ZERO SOLUTION.

The general solution of 4.7 is

$$m^2 = \frac{1}{2d}\left(-c \pm \sqrt{c^2 - 4db_0(T - T_c)}\right) \tag{4.9}$$

If $T > T_c$ both roots are negative (remember $c > 0$) and m is not real. This is not a physical solution and hence for $T > T_c$ the equilibrium state of the system has $m = 0$. For $T < T_c$, only one of the roots is positive and we find

$$m^2 = \frac{1}{2d}\left(\sqrt{c^2 + 4db_0(T_c - T)} - c\right) \tag{4.10}$$
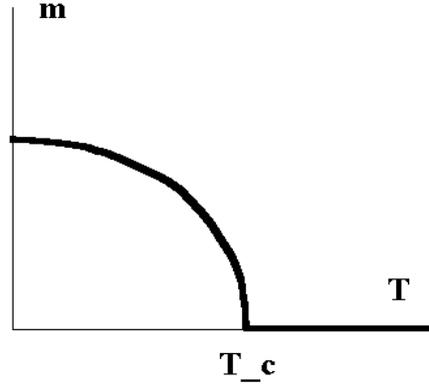
Figure 4.6: **Magnetization versus temperature.**

or

$$m^2 = \frac{c}{2d}\left(\sqrt{1 + \frac{4db_0}{c^2}(T_c - T)} - 1\right) \tag{4.11}$$

In the limit $T \uparrow T_c$, we can use $\sqrt{1+x} - 1 \approx \frac{1}{2}x$, and the values for the magnetic moment are

$$m = \pm\sqrt{\frac{b_0}{c}}\sqrt{T_c - T} \tag{4.12}$$

which is shown in figure 4.6. Experiments show a very similar behavior, except that the general form is

$$m \propto (T_c - T)^\beta \tag{4.13}$$

where typical values of β are around 0.33 in stead of 0.5 found in our Landau model. Therefore the magnetization is qualitatively correct in the Landau model (for example, it goes to zero without a jump), but the exponent is wrong. For such quantitative details it is clearly important to know what happens at the phase transition in terms of fluctuations, and Landau's theory is too simplistic, as mentioned before, because it ignores fluctuations .

FREE ENERGY PICTURES.

A picture of the Helmholtz free energy as a function of m looks like figure 4.7. The analysis of these curves is easy. In the limit of infinite magnetization the curves go to positive infinity. At m=0 the curves have either a maximum or a minimum. There are two cases. For $T > T_c$ there is only one extremum, and this has to be the point m=0, which therefore has to be a minimum. For
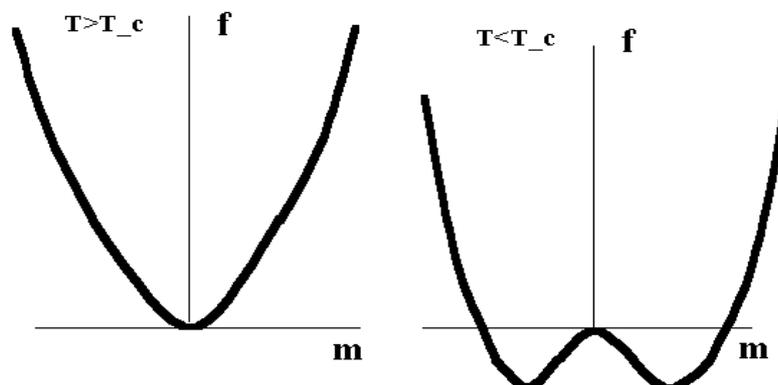
Figure 4.7: **Forms of the Helmholtz free energy.**

$T < T_c$ there are three extrema, one at zero, one positive, and one negative. Therefore, the point m=0 has to be a maximum, and the minima are at the symmetric non-zero points.

Since we are dealing with a fifth order equation, could we have the sequence minimum, maximum, minimum, maximum, minimum for the extrema?

RESPONSE FUNCTIONS.

One of the important response function for our simple T system is the heat capacity. The heat capacity is related to the partial derivative of the entropy. Since volume in our model is not a state variable which can be varied, there is only one heat capacity and it is related to the free energy via:

$$C = -VT\frac{d^2 f}{dT^2} \tag{4.14}$$

Since temperature is the only external state variable, there are no partial derivatives. The free energy is

$$T > T_c : f(T) = a(T) \tag{4.15}$$

$$T < T_c : f(T) = a(T) + \frac{1}{2}b_0(T - T_c)m^2 + \frac{1}{4}cm^4 + \frac{1}{6}dm^6 \tag{4.16}$$

Near T_c both the second and the third term in 4.16 are proportional to $(T-T_c)^2$. Near T_c the higher order terms do not play a role, since they are proportional to larger powers of $T - T_c$. Hence f is approximated by
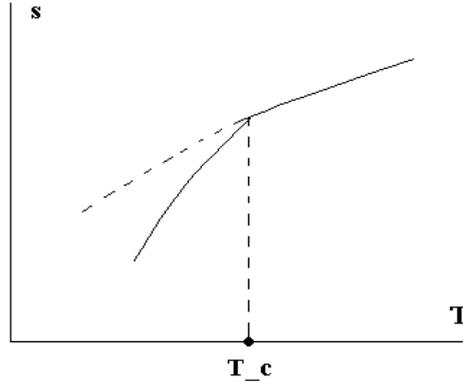
Figure 4.8: **Entropy near the critical temperature.**

$$T \uparrow T_c : f(T) \approx a(T) - \frac{1}{4}\frac{b_0^2}{c}(T - T_c)^2 \qquad (4.17)$$

The entropy per unit volume, $s = \frac{S}{V} = -\frac{df}{dT}$ and follows from

$$T > T_c : s(T) = -\frac{da}{dT}(T) \qquad (4.18)$$

$$T < T_c : s(T) = -\frac{da}{dT}(T) + \frac{b_0^2}{2c}(T - T_c) \qquad (4.19)$$

which has the behavior as shown in figure 4.8. The specific heat per unit volume follows from $c = \frac{C}{V} = T\frac{ds}{dT}$ and is given by

$$T > T_c : c(T) = -T\frac{d^2 a}{dT^2}(T) \qquad (4.20)$$

$$T < T_c : c(T) = -T\frac{d^2 a}{dT^2}(T) + T\frac{b_0^2}{2c} \qquad (4.21)$$

which is shown in figure 4.9. This is the same type of behavior as found in the van der Waals model, where the heat capacity also jumps. There is no divergent behavior, however, as seen in many experiments. This is again related to the fact that we did not include fluctuations. We have a homogeneous system with m independent of time and position.

RELATIONS ACROSS T_c.

The Landau model relates the free energy below and above the transition temperature, and leads to two distinct analytical forms in these regions, with discontinuities. This is similar to the van der Waals model of a phase transition.
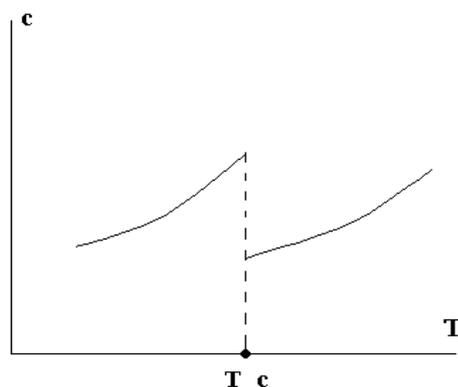
Figure 4.9: **Specific heat near the critical temperature.**

The difference, however, is in the origin of the energy relation. In stead of modelling an equation of state, we have a model for the Helmholtz free energy that is valid everywhere, but selects a different minimum in the different regions. This approach can be connected to more detailed models in an easier way, since it is more fundamental.

The term related to a(T) is always present and gives a contribution to s and C which is continuous at the phase transition. The second term in the free energy for the ordered phase leads to a discontinuity in the slope of s, and the heat capacity jumps by an amount $VT_c \frac{b_0^2}{2c}$. The entropy has an additional term $\frac{b_0^2}{2c}(T - T_c)$ for temperatures below T_c. Hence the entropy in the ordered state is less than the entropy in the state with $m = 0$. This is in agreement with our intuitive notion of entropy as a measure of the internal randomness of a system. The ordered state has lower entropy.

Since the entropy is lower in the ordered state, why does the maximum entropy principle not imply that the disordered state should be the stable state?

SUSCEPTIBILITY.

Very often it is easier to measure the magnetic susceptibility in stead of the magnetization density itself. This is due to the fact that it is often easier to do a differential measurement. By definition $\chi_T(T, M) = \left(\frac{\partial M}{\partial H}\right)_T$ and $\chi_T^{-1}(T, M) = \left(\frac{\partial^2 F}{\partial M^2}\right)_T$. Hence we find that

$$\chi_T^{-1}(T, M) = V^{-1}\left(b_0(T - T_c) + 3cm^2 + 5dm^4\right) \tag{4.22}$$
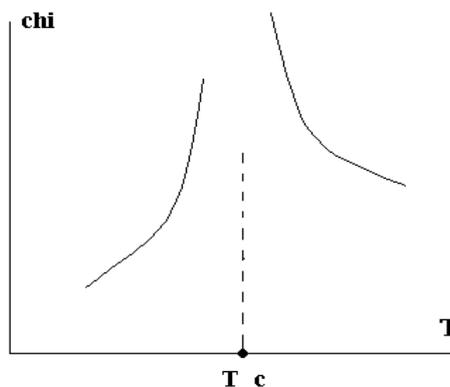
Figure 4.10: **Magnetic susceptibility near the critical temperature.**

If we now use the solutions for m(T) we find

$$T > T_c : \chi_T(T) = \frac{V}{b_0(T - T_c)} \tag{4.23}$$

$$T < T_c : \chi_T(T) = \frac{V}{2b_0(T_c - T)} \tag{4.24}$$

This response function is sketched in the figure 4.10. Note that the susceptibility diverges at the critical point. The nature of the divergence is the same at each side of the transition, here a power of minus one in both cases. The exponent is the same. This is a general characteristic which we will discuss more in the next chapter. The pre-factors are different, though, and in this case the low temperature form has an extra factor of two.

4.5   Order of a phase transition.

One of the basic ways to distinguish phase transitions is by looking at the change in order parameter at the critical temperature. If the value of the order parameter jumps from one value to another, and hence is discontinuous, the phase transition is called <u>first order</u>. If this is not the case, the phase transition is called of second order. It is actually possible to even further distinguish the order of phase transitions, although perhaps not very useful. One way is to consider the functions $\left(\frac{\partial^n F}{\partial T^n}\right)$ as a function of temperature near T_c. The order of the phase transition is then given by the lowest value of n for which this partial derivative is discontinuous. Our previous example would be of second order in that case.

4.6 Second case: first order transition.

In the general form of the Landau expansion, equation 4.3, for a symmetric model, we can typically assume that the lower order terms are the most important and have the most important temperature dependence. The term a(T) is always present and gives a continuous background contribution. If all the other terms are positive, then the state with m=0 is the only state corresponding to a minimum of the free energy. Therefore, in order to see some interesting behavior, at least on term should change sign as a function of temperature, or be negative at all temperatures. The easiest case is when the term b(T) changes sign. Here we study the next important case. Other fun cases are treated in the problems.

NEGATIVE SIGN IN FOURTH ORDER TERM.

This very interesting case is obtained when we assume that $b(T) > 0$, $c(T) = c < 0$, $d(T) = d > 0$, and all other coefficients are zero. We also assume that the dominant temperature dependence is in the b(T) term, and have indeed set the higher order terms to be constant. In order to see interesting behavior like normally observed, we assume that $\frac{db}{dT} > 0$. Since $b(T) > 0$ the point $m = 0$ will always correspond to a local minimum of the Helmholtz free energy. It might, however, not be the global minimum. Because $c < 0$ it is possible that the free energy curve bends down and goes through a maximum as a function of m. In that case there has to be another minimum in the free energy as a function of m, since $d > 0$ implies that for very large values of m the free energy approaches plus infinity. Three possible forms of the Helmholtz free energy as a function of m are shown in figure 4.11.

Why don't we have the sequence minimum, maximum, minimum in the free energy as a function of the order parameter?

We again construct the partial derivatives of the Helmholtz free energy:

$$\left(\frac{\partial f}{\partial m}\right)_T = b(T)m + cm^3 + dm^5 \tag{4.25}$$

$$\left(\frac{\partial^2 f}{\partial m^2}\right)_T = b(T) + 3cm^2 + 5dm^4 \tag{4.26}$$

The solutions for m are

$$m = 0 \tag{4.27}$$
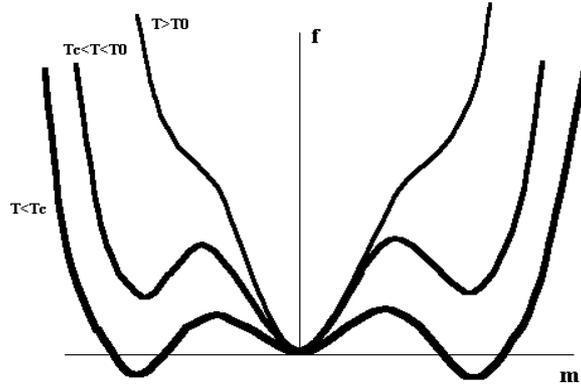
Figure 4.11: **Three possible forms of the Helmholtz free energy in case 2.**

$$m^2 = \frac{-c \pm \sqrt{c^2 - 4b(T)d}}{2d} \qquad (4.28)$$

Hence if $4b(T)d > c^2$ only $m = 0$ is a solution. In that case the fourth order term in the expansion of the Helmholtz free energy is not strong enough to pull the function down to a second minimum. In the other case we find two extrema. Note that in this case the two possible values for m^2 are always real, and hence the values of m are always real. The argument in the previous paragraph shows that the extremum closest to $m^2 = 0$ corresponds to a maximum, and the other one to a minimum. In order to obtain a value for m pertaining to that second minimum we need to take the plus sign in 4.28. A picture of the solutions for m^2 is given in figure 4.12, where the temperature T_0 follows from $4b(T_0)d = c^2$. The values for m^2 at this temperature are $m^2(T_0) = \frac{-c}{2d}$. Since b(T) is increasing with temperature, the non-zero solution only plays a role for $T < T_0$.

ENERGY DIFFERENCE.

The important question, when there are more minima, is to determine which state corresponds to a global minimum. The difference in free energy is again

$$f(T, m) - f(T, 0) = \frac{1}{2}b_0(T - T_c)m^2 + \frac{1}{4}cm^4 + \frac{1}{6}dm^6 =$$

$$\frac{1}{2}\langle b_0(T - T_c) + cm^2 + dm^4 \rangle m^2 - \frac{1}{4}cm^4 - \frac{1}{3}dm^6 \qquad (4.29)$$

and the term in brackets is zero at a minimum. Since $c < 0$ the difference in free energy can either be positive or negative and the sign of the difference is determined by the sign of $c + \frac{4}{3}dm^2$. If the value of m^2 for the minimum is small, the term with c will dominate and the free energy for the $m = 0$ solution
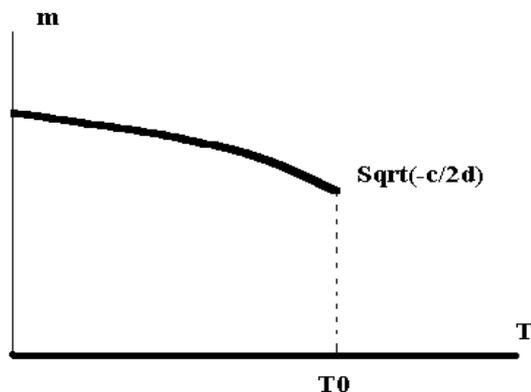
Figure 4.12: **Values for m corresponding to a minimum in the free energy.**

is the lowest. Substituting the solution for m in the difference of the free energy values we find

$$\Delta F = -\frac{1}{12}m^4 \left(c + 2\sqrt{c^2 - 4b(T)d} \right) \tag{4.30}$$

The function b(T) is an increasing function of temperature, and for large values of the temperature (but always keeping $4b(T)d < c^2$) the term in brackets is determined mainly by c and the difference in the free energy is positive (remember that c is negative). In that case $m = 0$ is the stable state. For small values of the temperature, if b(T) becomes small enough, the term in brackets will change sign and the state with non-zero magnetic moment is stable.

CRITICAL TEMPERATURE.

Since we assume that b(T) is monotonous, there will only be one value of the temperature for which the difference in free energy is zero. This critical temperature is determined by

$$c + 2\sqrt{c^2 - 4b(T)d} = 0 \tag{4.31}$$

or

$$b(T_c) = \frac{3c^2}{16d} \tag{4.32}$$

At the phase transition the value of the order parameter jumps from zero to m_c which is given by

$$m_c = \sqrt{-\frac{3c}{4d}} \tag{4.33}$$
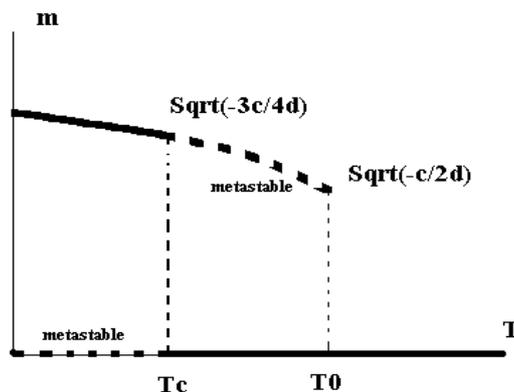
Figure 4.13: **Magnetization as a function of temperature.**

This transition is therefore of first order.

ANALYSIS OF THE TRANSITION.

The complete plot of the value of the magnetization density as a function of temperature is given in figure 4.13. There are some important conclusions to be drawn. If we start at low temperature in a magnetized state and heat the system slowly, we will follow the meta-stable magnetic state even above T_c if we do things very carefully. This is because in order to go to the stable non-magnetic state the system first has to increase its energy. There is an energy barrier. This is very typical for a first order phase transition. A system in this case can be superheated or under-cooled into a meta-stable state. The further we are in the meta-stable region, the easier it is to perturb the system and force it to go to the stable state. The detailed mechanism of such phase transitions is often described in the framework of nucleation and growth. One needs to know how small seeds of the stable phase can form through fluctuations and how they can expand by growing. Clearly, in a solid this is a much slower process than in a liquid, since the motion of atoms in a solid is very slow.

HYSTERESIS.

When we perform a real experiment in which we bring a system through a first order phase transition we always do the experiment at a measurable speed, never reversibly slow. Therefore, we will always bring the system into the meta-stable state before it transforms to the stable state. This is called hysteresis, see figure 4.14. The amount by which we can bring the system into the meta-stable state depends on the material we study. If nucleation and growth is slow, this can be quite far. Typically, nucleation is a thermal process with
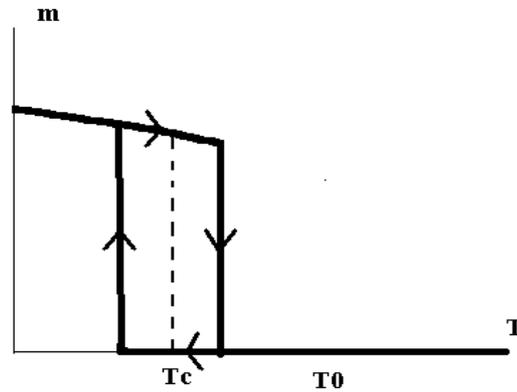
Figure 4.14: **Hysteresis loop.**

probability inversely proportional to a Boltzmann factor, or exponential in the energy difference between the states. Therefore, the probability of transforming becomes exponentially small near the critical temperature in such a model. As a consequence, reducing the speed of the process by a factor of two does not reduce the width of the hysteresis loop by a factor of two, but only by a small amount. This is of great importance in many applications related to magnetism or phase transitions in crystal structures.

What do you expect to happen for hysteresis loops for very small samples?

DISCONTINUITIES.

In the first order phase transition discussed here the order parameter m jumps in value at the critical point. Since we switch from one minimum to another in the free energy curve, the change in free energy with temperature will in general be different in the two states. Hence $\frac{df}{dT}$ will also be discontinuous at the critical points, and hence the entropy jumps in value. This is completely different in a second order phase transition, where both m and S are continuous. Since m is continuous, there is also no hysteresis in a second order phase transition.

SUSCEPTIBILITY.

The susceptibility is obtained from $\chi_T^{-1}(T, M) = \left(\frac{\partial^2 F}{\partial M^2}\right)_T$ and is:

$$T > T_c : \chi_T(T) = \frac{V}{b(T)} \tag{4.34}$$

$$T < T_c : \chi_T(T) = \frac{V}{b(T) + 3cm^2 + 5dm^4} = \frac{V}{2m^2(T)\left(c + 2dm^2(T)\right)} \tag{4.35}$$

Since b(T) is positive and increasing, the susceptibility above T_c is decreasing. Also 4.28 shows that m(T) is a decreasing function of T, and hence the susceptibility is an increasing function of temperature below T_c. Note that $c + 2dm^2$ is always positive.

ENTROPY.

The entropy as a function of temperature follows from $s = -\left(\frac{\partial f}{\partial T}\right)_m -$ $\left(\frac{\partial f}{\partial m}\right)_T \frac{dm}{dT}$. The derivatives of m versus temperature do not play a role, since $\left(\frac{\partial f}{\partial m}\right)_T = 0$. Hence we find

$$T > T_c : S(T) = -\frac{da}{dT} \tag{4.36}$$

$$T < T_c : S(T) = -\frac{da}{dT} - \frac{1}{2}\frac{db}{dT}m^2(T) \tag{4.37}$$

Since b(T) is an increasing function of T, the entropy in the ordered state is again lower than the entropy in the disordered state, as expected. This is not in disagreement with the statement in chapter one, where we concluded that the entropy has to be a maximum, since that statement pertains to a situation of *constant internal energy*, and here the internal energy is different in the two states. If we assume that b is linear in T, the heat capacity in the ordered phase differs from the heat capacity in the $m = 0$ phase by a term $-\frac{db}{dT}m(T)\frac{dm}{dT}$ and this is a positive term which does not diverge at T_c. The behavior of these quantities near T_c is sketched in figure 4.15.

BASIC DIFFERENCE IN BEHAVIOR.

We have studied the description of a first order phase transition and of a second order phase transition. The stable state of the system is associated with the global minimum in the free energy. The position of such a minimum depends on an external control variable, like the temperature. If as a function of the temperature the global minimum changes position by an interchange in a global-local minimum pair, the transition is first order. On the other hand, in a second order phase transition the global minimum becomes a maximum and in this process two minima are created on either side. This gives an important difference, which we have to keep in mind when we construct models for
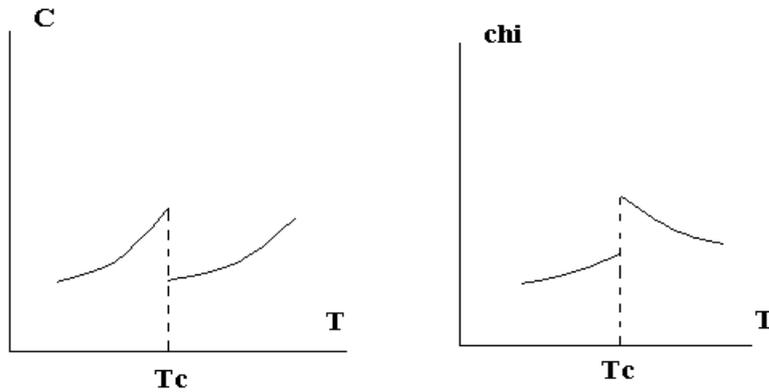
Figure 4.15: **Critical behavior in first order phase transition.**

phase transitions. In a first order transition both states are available at either side of the transition, but in a second order transition new states are created. Therefore, hysteresis never occurs in a second order phase transition!

COMBINED BEHAVIOR.

In real materials we see often combined types of behavior. For example, a transition could be second order in temperature like in our magnetic case. If we now work at a temperature below the critical temperature and apply a magnetic field, we see a first order transition in which the magnetization flips from one direction to the opposite direction. But this first order transition is clearly related to what happens at the critical point. In fact, the Landau model for a range around the critical point is given by the model in our first case. It makes therefore more sense to distinguish continuous phase transitions (ending in a critical point) from discontinuous transitions, and model the behavior accordingly.

4.7 Fluctuations and Ginzburg-Landau theory.

FLUCTUATIONS NEAR A PHASE TRANSITION.

The phenomenological theory of Landau has been very useful in classifying the order and nature of phase transitions. But the form 4.3 of the free energy is incomplete near a phase transition. We know that near a phase transition fluctuations are important. For example, if we watch water boil, we see that vapor bubbles form near the bottom of a pan. Gravity will send these bubbles up. Since inside these bubbles the pressure is too low, they will collapse. Closer

to the boiling point we will see both more bubbles forming, and larger bubbles forming. Especially near the critical point, one finds very large bubbles!

How to deal with these?

In order to study fluctuations we need non-equilibrium thermodynamics. We need to study a system that is not uniform in space, and also changes over time. This is a difficult task. Ginzburg, however, found a very good first step to include spatial non-uniformity. He started from Landau's model. He still assumed that the problem was static, but allowed for spatial variations in the order parameter. In the approach studied here we do not discuss the origin of the driving forces towards non-uniformity, we simply assume that they exist. We also ignore surface tension, which certainly plays a role, and simply assume that the effects of surface tension are incorporated in the values of the parameters in our model.

Divide and conquer.

To understand the origin of our problem, we divide the volume of the total system in a large number of much smaller systems with a much smaller volume. On one hand, the number of small sub-systems is very large, but these sub-systems themselves are still large enough to be considered to be macroscopic, e.g. they contain many atoms. All these small sub-systems are in thermal contact. All sub-systems are in thermal equilibrium. The total system is in thermal equilibrium and the average of the internal energy of each subsystem is a fixed value and the same everywhere. But the internal energy for a small sub-system may vary. The larger the deviation from the average value, the more unlikely the fluctuation. In this sense we consider the total system to be an ensemble of small systems in thermal contact.

What is a vapor bubble containing one atom?

Position dependent order parameter.

If the system is far away from a phase transition, all sub-systems will be in the same phase. If the total system is very close to a phase transition, about half of the sub-systems will have state variables which correspond to a meta-stable thermodynamical state. These sub-systems try to change phase until they have exchanged enough energy with the neighboring sub-systems, in which case they correspond to a stable state again. In terms of the order parameter the following description arises. A subsystem at position $\vec{r}$ has its own order parameter $m(\vec{r})$. The average value of the order parameter, $\int m(\vec{r})d^3r$, is equal

to the order parameter M for the total system and can be calculated from the values of the state variables for the total system. Near a phase transition, there are large fluctuations in $m(\vec{r})$, however. Because our sub-systems contain many atoms, this implies that variations in $m(\vec{r})$ are on a length scale much larger than the inter-atomic distance, but possibly small compared to the sample size. Note that for a homogeneous system we have $m(\vec{r}) = m$ and M=mV indeed.

How does this description of the order parameter compare with the definition of fields like $\vec{E}(\vec{r})$ in electromagnetism?

ENERGY CONSIDERATIONS.

Ginzburg and Landau improved the phenomenological theory discussed before by including these fluctuations. They assumed that the states of neighboring sub-systems are close together and that $m(\vec{r})$ varies slowly. In that case the fluctuations are taken into account by adding terms in the free energy which contain derivatives of $m(\vec{r})$. Precisely at the phase transition this will still be incorrect, since the order parameter or its slope varies in a discontinuous manner, and $m(\vec{r})$ is not analytical. An expansion of the free energy in terms of gradients of the order parameter is not valid near T_c and the improved Ginzburg-Landau theory is still not strictly valid near T_c. Nevertheless, it is a very useful theory, because it will be a good description of the state of a system much closer to the critical temperature than the previous Landau theory.

FORMAL THEORY.

The Helmholtz free energy is in Ginzburg-Landau theory given by an integration over all space. As an example, we will extend our model of a second order phase transition to include fluctuations. In that case we write

$$F(T, m(\vec{r})) = \int d^3r \left(a(T) + \frac{1}{2}b_0(T - T_c)m^2(\vec{r}) + \frac{1}{4}cm^4(\vec{r}) + \frac{1}{6}dm^6(\vec{r}) \right)$$

$$+ \frac{1}{2}f \int d^3r \left| \vec{\nabla}m(\vec{r}) \right|^2 \tag{4.38}$$

with b_0, c, d, and f all positive. When the magnetic moment is homogeneous, $m(\vec{r}) = \frac{M}{V}$, this expression is the same as we studied before, except for a redefinition of the coefficients a, b, c, and d by factors of powers of the volume. The last term in 4.38 represents fluctuations in the order parameter. The coefficient f has to be positive, else the system would be unstable against fluctuations. With a positive value of f we see that it costs energy to create a fluctuation, as

expected. Assuming that we have an isotropic system, the free energy cannot depend on the direction of $\vec{\nabla}m$, and the form 4.38 is the simplest choice we can make.

FUNCTIONAL DERIVATIVES DERIVED.

How does the Helmholtz free energy 4.38 change when the order parameter changes by a small amount $\delta m(\vec{r})$? We need to calculate $\delta F(T, m(\vec{r})) = F(T, m(\vec{r}) + \delta m(\vec{r})) - F(T, m(\vec{r}))$. If the change in the order parameter is small, we only need to keep first order terms, and obtain

$$\delta F(T, m(\vec{r})) = \int d^3r \delta m(\vec{r}) \left(b_0(T - T_c)m(\vec{r}) + cm^3(\vec{r}) + dm^5(\vec{r}) \right)$$

$$+f \int d^3r \vec{\nabla}m(\vec{r}) \cdot \vec{\nabla}\delta m(\vec{r}) \tag{4.39}$$

The last term is equal to

$$-f \int d^3r \delta m(\vec{r})\vec{\nabla}^2 m(\vec{r}) + f \oint d^2\sigma \delta m(\vec{r})\hat{n}(\vec{r}) \cdot \vec{\nabla}m(\vec{r}) \tag{4.40}$$

The surface integral vanishes for a finite sample, since in that case $m(\vec{r}) = 0$ outside the sample. This integral also vanishes if we employ periodic boundary conditions. The fluctuations in the free energy are therefore:

$$\delta F(T, m(\vec{r})) = \int d^3r \delta m(\vec{r}) \left(b_0(T - T_c)m(\vec{r}) + cm^3(\vec{r}) + dm^5(\vec{r}) - f\vec{\nabla}^2 m(\vec{r}) \right) \tag{4.41}$$

POSITION DEPENDENT MAGNETIC FIELD.

If we consider the magnetization as a external state variable, the magnetic field needed to cause a magnetization $m(\vec{r})$ is found by generalizing $H = \left(\frac{\partial F}{\partial M}\right)_T$ to a functional derivative

$$h(\vec{r}) = \left(\frac{\delta F}{\delta m}\right)_T \tag{4.42}$$

which is equivalent to

$$\delta F = \int d^3r \delta m(\vec{r})h(\vec{r}) \tag{4.43}$$

and which leads to

$$h(\vec{r}) = b_0(T - T_c)m(\vec{r}) + cm^3(\vec{r}) + dm^5(\vec{r}) - f\vec{\nabla}^2 m(\vec{r}) \tag{4.44}$$

by construction from equation 4.41. This equation is a typical differential equation. The term with the Laplace operator occurs in many different places. The difference with other often studied second order differential equations is the fact that equation 4.41 is non-linear.

Spontaneous solutions.

A spontaneous magnetization is possible when this equation has solutions for $h(\vec{r}) = 0$, and this gives us exactly the situation we discussed before. When $h(\vec{r}) = 0$ fluctuations will increase the free energy (this follows directly from equation 4.38) and the ground state corresponds to a homogeneous magnetization $m(\vec{r}) = \frac{M}{V}$. Equation 4.44 then reduces to the form we solved before, leading to the same second order phase transition.

Response to a driving force.

The easiest way to study fluctuations is to consider $m(\vec{r})$ as an external state variable and ask the question how the system responds to certain kinds of external fields $h(\vec{r})$. This is like in resonance situations, where we ask which driving force gives the largest response. For example, an interesting situation arises when we use $h(\vec{r}) = h_0\delta(\vec{r})$. The system is locally perturbed and one would like to know how far away the effects of this perturbation can be seen. In terms of the sub-systems we introduced before, this means that we change the state of one sub-system away from the average by applying a external magnetic field, and we want to know how the other sub-systems respond. The use of a Dirac delta-function is mathematically justified if we assume that it is possible to divide the large total system in a very large number of sub-systems. One can think of this by considering a delta function in the limit of a very narrow Gaussian, for example.

What could be the cause of such a small external force?

Small external force.

We will assume that h_0 is small, and that the resulting magnetization $m(\vec{r})$ is close to the value without an external field, $m(\vec{r}, T) = m_0(T) + \phi(\vec{r}, T)$. The function ϕ will also be small. We are interested in changes in the magnetization near the critical point, when the magnetization itself is small. To simplify the mathematics we will therefore ignore the sixth order term, which is small in this region. In other words, we set $d = 0$. We then know that

$$0 = b_0(T - T_c)m_0(T) + cm_0^3(T) \tag{4.45}$$

which has the solutions $m_0(T) = 0$ for $T > T_c$ and $m_0(T) = \sqrt{\frac{b_0(T_c-T)}{c}}$ for $T < T_c$. This equation is subtracted from the equation 4.44 determining $m(\vec{r}, T)$ and only terms linear in ϕ are retained. Note that mathematically it is possible to have solutions with large values of ϕ, essentially given by $c\phi^3 - f\vec{\nabla}^2\phi = 0$, but such solutions also imply fast variations of ϕ which is physically not possible because of the atomic structure of matter. As a result we get

$$h_0\delta(\vec{r}) = b_0(T - T_c)\phi(\vec{r}, T) + c3m_0^2(T)\phi(\vec{r}, T) - f\vec{\nabla}^2\phi(\vec{r}, T) \qquad (4.46)$$

The second term on the right is different above and below T_c. Using the solution for $m_0(T)$ gives us

$$T > T_c : \vec{\nabla}^2\phi(\vec{r}, T) - \frac{b_0(T - T_c)}{f}\phi(\vec{r}, T) = -\frac{h_0}{f}\delta(\vec{r}) \qquad (4.47)$$

$$T < T_c : \vec{\nabla}^2\phi(\vec{r}, T) + 2\frac{b_0(T - T_c)}{f}\phi(\vec{r}, T) = -\frac{h_0}{f}\delta(\vec{r}) \qquad (4.48)$$

SOLUTION AWAY FROM ORIGIN.

First we consider the differential equation at all points away from the origin. In that case the equation has the form:

$$\vec{\nabla}^2\phi + \alpha\phi = -\frac{h_0}{f}\delta(\vec{r}) = 0 \qquad (4.49)$$

with $\alpha < 0$, which can be solved easily. The solutions are of the form

$$\frac{1}{r}u_l(r)Y_{lm}(\Omega) \qquad (4.50)$$

because the system has rotational symmetry. Since fluctuations increase the energy, the energy will be the lowest when ϕ has spherical symmetry, and hence we need to exclude all terms but the l=0 term. Therefore, $\phi = \frac{u(r)}{r}$ (the factor $\sqrt{4\pi}$ from the spherical harmonic is now included in the radial function u) and we need to solve

$$u'' + \alpha u = 0 \qquad (4.51)$$

which has the solution $u = e^{\pm\imath\sqrt{\alpha}r}$. Since the total response has to be calculated from $\int \phi d^3r$ we discard the increasing solution and we get $\phi = \frac{A}{r}e^{-\frac{r}{\xi}}$, where $\xi\sqrt{\alpha} = \imath$.

EFFECTS OF THE ORIGIN.

The effects of the delta function singularity at the origin are taken into account by integrating the equation

$$\vec{\nabla}^2\phi + \alpha\phi = -\frac{h_0}{f}\delta(\vec{r}) \tag{4.52}$$

over a sphere of radius R around the origin, and then take the limit $R \to 0$. That leaves us with

$$\int_{r<R} \vec{\nabla}^2\phi d^3r + \int_{r<R} \alpha\phi d^3r = -\frac{h_0}{f} \tag{4.53}$$

The first integral is

$$\int_{r<R} \vec{\nabla}^2\phi d^3r = \oint_{r=R} \vec{\nabla}\phi \cdot \hat{n}d^2S = 4\pi R^2 \left.\frac{d\phi}{dr}\right|_{r=R} \tag{4.54}$$

where $\frac{d\phi}{dr}$ is equal to $-\frac{A}{R^2}e^{-\imath\sqrt{\alpha}R} + \frac{A\imath\sqrt{\alpha}}{R}e^{-\imath\sqrt{\alpha}R}$. In the limit $R \to 0$ only the first part survives. Also, in this limit the term $\int_{r<R} \alpha\phi d^3r$ goes to zero, and we are left with

$$-4\pi A = -\frac{h_0}{f} \tag{4.55}$$

and therefore the general solution for our problem is in terms of ξ:

$$\phi(\vec{r}, T) = \frac{h_0}{4\pi f r}e^{-\frac{r}{\xi}} \tag{4.56}$$

with

$$T > T_c : \xi(T) = \sqrt{\frac{f}{(T - T_c)b_0}} \tag{4.57}$$

$$T < T_c : \xi(T) = \sqrt{\frac{f}{2(T_c - T)b_0}} \tag{4.58}$$

INTERPRETATION OF THE RESULTS.

The interpretation of the solution is very interesting. If the magnetization m at the origin deviates from the equilibrium value, this will create a local magnetic field. This local magnetic field will perturb the magnetization everywhere. The effects of such a change decay exponentially and are essentially localized within a sphere of radius ξ. The length ξ is called the correlation length. The correlation length gives the distance over which perturbations have a noticeable effect.

Also, the correlation length ξ does not depend on the strength h_0 of the perturbation. This indicates that the correlation length ξ is a real system parameter which does not depend on the outside world.

The perturbation is also proportional to the local magnetic field, as expected in our simple calculation where we only included linear terms. For small fluctuations this is certainly justified. If the external field is zero, the response is zero, as expected.

The perturbation is inversely proportional to f, the factor scaling the energy related to fluctuations. When f is large, fluctuations in the magnetization cost a lot of energy and are more unlikely. ϕ is indeed small in that case. Amazingly, the correlation length is proportional to $\sqrt{f}$. If in a system f is large, fluctuations are small, but they have a very large range! On the other hand, if f approaches zero, all fluctuations are essentially localized since ξ approaches zero, but the fluctuations themselves can be very large. In other words, when it is easy to cause a perturbation, this perturbation is also screened rapidly because the system can also generate a response easily.

Note that in the Ginzburg-Landau theory we merely explain what happens to a system when a fluctuation occurs. We do not explain why fluctuations occur, and how instabilities might arise. We only discovered a theory that shows why fluctuations are screened and how we can measure that screening.

Divergence at T_c.

The most important feature of the equations for the correlation length is the fact that in the limit $T \to T_c$ the correlation length diverges. Near a phase transition any small change in the magnetization at one point will be noticeable all over the sample. This is an example of the inherent instability of a system at a phase transition. Note that the nature of the divergence is the same when we approach the critical temperature from below or from above. Both go like the square root of the temperature difference. The pre-factors are not the same, however, and in our case they differ by a factor of $\sqrt{2}$.

4.8   Extra equations.

1. *Why do we work with the Helmholtz free energy and not Gibbs?*

2. *Why is there a peak in the heat capacity?*

3. *Give examples of order parameters.*

4. *How do you measure the value of the order parameter?*

5. *Why are there no phase transitions in a finite system?*

6. *Discuss the relation between correlation length versus system size.*

7. *What is broken symmetry?*

8. *To get f(t,m) from F(T,M,N), what did we use?*

9. *When do power series converge?*

10. *Why does Landau's theory imply some kind of universality?*

11. *Why is Landau more fundamental than using an EOS?*

12. *Work out the results for a second order transition with $d = 0$*

13. *Would a theory with $b(T) > 0$ and $c(T)$ changing sign give a phase transition?*

14. *Work out results for $b = 0$, c changing sign, d positive.*

15. *Why do we go from something of the form (T,m) to (T), and what happened with the additional degree of freedom?*

16. *Using the free energy pictures, analyze the nature of phase transitions.*

17. *Is hysteresis equilibrium?*

18. *Can we under-cool a gas?*

19. *If magnetic phase transitions are second order, why do we see hysteresis loops?*

20. *Why is the gradient term the lowest order and the only second order term?*

21. *What are functional derivatives?*

22. *What does it mean that the correlation length diverges at the critical temperature?*

23. *Interpret the meaning of formula 4.56*

24. *Do correlations decay at the critical temperature?*

25. *Is it significant that the scaling is the same at both sides of the critical temperature.*

4.9 Problems for chapter 4

PROBLEM 1.

Suppose that in the expansion for the Helmholtz free energy per unit volume $f = \frac{F}{V}$ as a function of the magnetization density $m = \frac{M}{V}$ a third order term is present. This is possible in systems consisting of large anisotropic molecules. The free energy in this case is

$$f(m, T) = a(T) + \frac{1}{2}b(T)m^2 + \frac{1}{3}c(T)m^3 + \frac{1}{4}d(T)m^4$$

Assume that $b(T) = b_0 * (T - T_0)$ and $b_0 > 0$, $c(T) = c < 0$, and $d(T) = d > 0$.

(a) Show that this system exhibits a first-order phase transition at a temperature T_c.

(b) Calculate T_c in terms of b_0, T_0, c, and d.

(c) Calculate $\lim_{T \uparrow T_c} m(T)$.

PROBLEM 2.

In this chapter we have only considered the temperature as a state variable driving a phase transition. Suppose the pressure is also important. The Helmholtz free energy per unit volume is then given by

$$f(m, p, T) = a(p, T) + \frac{1}{2}b(p, T)m^2 + \frac{1}{4}c(p, T)m^4 + \frac{1}{6}d(P, T)m^6$$

where we ignored all higher order terms. Assume that $d(p, T) = d > 0$.

(a) If $c(p, T) = c > 0$, give an expression which determines T_c as a function of pressure for a second order phase transition.

(b) If $c(p, T) = c < 0$, $b(p, T) > 0$, and b(p,T) increases as a function of temperature, give an expression which determines T_c as a function of pressure for a first order phase transition.

(c) Suppose $b(p, T) = b_0 p(T - T_0)$ and $c(p, T) = c_0 T(p - p_0)$, with $b_0 > 0$ and $c_0 > 0$. Sketch in a p-T diagram the function $T_c(p)$ for both the first order and the second order phase transition.

(d) Show that the two curves in part (c) connect at one point (called a tri-critical point) and that the derivatives of the curves are the same in this tri-critical point.

PROBLEM 3.

The Helmholtz free energy per unit volume for a two dimensional system is given by

$$f(m_x, m_y, T) = a(T) + \frac{1}{2}b(T)(m_x^2 + m_y^2) + \frac{1}{4}c(T)m_x^2 m_y^2 + \frac{1}{4}d(T)(m_x^4 + m_y^4)$$

Assume that $b(T) = b_0(T - T_c)$ with $b_0 > 0$, $c(T) = c > 0$ and $d(T) = d > 0$.

(a) Show that this system has a second order phase transition at T_c.

(b) If $c = 2d$, show that m(T) is like we derived in the text for a second order phase transition, but that m_x and m_y cannot be determined apart from the value for $m = \sqrt{m_x^2 + m_y^2}$.

(c) If $c \neq 2d$, show that $m_x = m_y$.

PROBLEM 4.

Discuss what happens in a Landau theory with $f(T; m) = a(T) + \frac{1}{2}b_0(T - T_0)m^2 + \frac{1}{4}cm^4 + \frac{1}{6}m^6$ and $b_0 > 0$, $c < 0$, and $d > 0$.

PROBLEM 5.

Discuss what happens in a Landau theory with $f(T; m) = a(T) + \frac{1}{4}c_0(T - T_0)m^4 + \frac{1}{6}m^6$ and $c_0 > 0$ and $d > 0$. Calculate the response functions.

PROBLEM 6.

Consider Ginzburg-Landau in d dimensions. Assume again a small perturbation of the form $h(\vec{r}) = h_0\delta(\vec{r})$ and look for a spherical solution. Show that the solutions for ϕ decay exponentially and that for small r ϕ diverges like r^{2-d}.

PROBLEM 7.

Calculate the latent heat for the first order phase transition discussed in the text.

PROBLEM 8.

A system is characterized by a three dimensional order parameter $\vec{S}$. The Landau expansion is

$$f(T; \vec{S}) = a(T) + \frac{1}{2}b_0(T - T_0)S^2 + \frac{1}{2}c_0(T - \frac{1}{2}T_0)(\hat{n} \cdot \vec{S})^2 + \frac{1}{4}dS^4$$

with $b_0 > 0$, $c_0 > 0$, $d > 0$ and $\hat{n}$ a constant unit vector. Discuss the phase transitions in this model.

PROBLEM 9.

The Helmholtz free energy per unit volume is given by

$$f(T;m) = R(T + \frac{1}{8}T_0)\cosh(\frac{2m}{m_0}) - RT_0\cosh(\frac{m}{m_0})$$

This models a phase transition. Calculate T_c. Is the transition first or second order?

PROBLEM 10.

The Helmholtz free energy per unit volume has the form

$$f(T;m) = a(T) + b_0(T - T_0)m\sqrt{m} + \frac{1}{4}cm^4$$

with $b_0 > 0$ and $c > 0$. We have introduced an unusual square root term. Show that this gives a second order phase transition and calculate the temperature dependence of the order parameter near the critical temperature.

PROBLEM 11.

Consider a model for a second order phase transition in a magnetic field. The Helmholtz free energy per unit volume is given by

$$f(T;m) = a(T) + \frac{1}{2}b(T)m^2 + \frac{1}{4}c(T)m^4$$

Assume $c(T) = c > 0$, a positive constant, and $b(T) = b_0(T - T_c)$ with $b_0 > 0$. The magnetization density is still considered to be an internal parameter, which should be chosen to minimize the Helmholtz free energy. The condition is now

$$\left(\frac{\partial f}{\partial m}\right)_T = H$$

Calculate m(T,H) (hint: use Maple or equivalent) and plot m(H) for various temperatures and m(T) for various fields.

PROBLEM 12.

Consider the following model of a tri-critical point:

$$f(m, T, p) = \frac{1}{2}a(T, p)m^2 + \frac{1}{4}b(T, p)m^4 + \frac{1}{6}cm^6$$

where c is a positive constant. The functions a and b are given by

$$a(T, p) = A\frac{T - T_c}{T_c} + B\frac{p - p_c}{p_c}$$

$$b(T, p) = C\frac{T - T_c}{T_c} + D\frac{p - p_c}{p_c}$$

Depending on the path in p-T space, along $p = f(T)$ with $p_c = f(T_c)$, the behavior of the response functions and the order parameter takes on a different form. For example, the behavior of the magnetization $m(p, T)$ always varies like $(T_c - T)^\beta$, but the value of β depends on the path taken. The two distinct regions with different values of β are called <u>critical</u> and <u>tri-critical</u>.

(A) Calculate the β this system.

(B) Draw the phase diagram in p-T space.

(C) Draw the critical and tri-critical regions in this phase diagram.

(D) Give an explanation of these results, write it in such a way that a new, incoming graduate student could understand it.

PROBLEM 13.

Consider the following model Helmholtz free energy per unit volume:

$$f(T; m) = a(T) + e^{\frac{T_0 - T}{T_0}} e^{-m^2} + ce^{m^2}$$

where $a(T)$ is an arbitrary function of temperature, and T_0 and c are positive constants. Show that this system undergoes a second order phase transition, calculate the critical temperature T_c, and find the critical exponent β.

PROBLEM 14.

A magnetic system has a spontaneous magnetization below a critical temperature T_c, given by $m^2 = m_0^2 \frac{T_c - T}{T_c}$. The system is in a state at temperature $T_i = 2T_c$ and magnetization $m_i = \frac{1}{2}m_0$. This system is cooled down to very low temperature, but at constant magnetization. Describe the state of the system at this very low temperature. Calculate relevant quantities as a function of temperature.

Chapter 5

Critical exponents.

5.1 Introduction.

CRITICAL POINT IS ESSENTIAL SINGULARITY.

In this chapter we will discuss the nature of second order phase transitions in more detail. Our language is a bit sloppy here, and by second order we really mean all phase transitions that end in a critical point. We have argued before that the behavior at the critical point determines what happens away from the critical point. Therefore, in this chapter we focus on properties at the critical point. Response functions will diverge, and near the critical point this divergent behavior overshadows any background behavior. It is not clear a priori, however, what near is. In terms on temperature, this could be 100K or 1μK.

What causes this divergent behavior?

What is meant by background?

DESCRIPTIONS OF BEHAVIOR AT THE CRITICAL POINT.

In chapter 3 we saw that we can model a phase transition if we know the Gibbs free energy for the two distinct phases. The coexistence curve was found by comparing these energies. In this scenario the Gibbs free energies of the two phases were quite uncorrelated, there was no hint that they actually came from

the same system. Near a phase transition, in many cases nothing diverged. We either were in one type of analytical behavior or in another. Landau theory improved on this by giving these two free energies a common origin. We defined

$$f_{equilibrium}(T) = \min_m f(T; m) \tag{5.1}$$

which related the free energy in each phase to a common model, which includes an internal parameter. This procedure again gave two distinct analytical forms of the free energy, one above and one below the transition. The nature of the construction of these model energies, however, now often introduces divergent behavior at the critical point.

CHARACTERIZATION OF THE SINGULARITIES.

Any realistic theory of a second order phase transition has to include the effects of fluctuations near the critical point. These fluctuations give rise to divergent behavior in response functions, and we therefore need to develop a mathematical description how to quantify differences in divergent behavior. The main characteristic of a divergence is the rate with which certain quantities go to infinity. This idea leads us then automatically to the idea of critical exponents, which are the parameters that show how fast the divergence is.

THE FOUR COMMON EXPONENTS.

We will define the four common critical exponents in terms of the model of a magnetic phase transition used before. This is just an easy way to describe what is happening, and similar procedures are valid for any second order phase transition. The order parameter for a second order phase transition approaches zero when the temperature approaches the critical temperature. Near the phase transition we have

$$T < T_c : m(T, H = 0) \propto (T_c - T)^\beta \tag{5.2}$$

The power β in this relation is called a critical exponent. Note that the relation above only holds when there is no applied external magnetic field.

If we apply a small magnetic field for a temperature equal to the critical temperature, we find another critical exponent δ:

$$H \to 0 : m(T = T_c, H) \propto H^{\frac{1}{\delta}} \tag{5.3}$$

The magnetic susceptibility $\chi = \left(\frac{\partial M}{\partial H}\right)_T$ also often diverges at T_c, due to the instability of a system near a phase transition.

Critical exponents γ and γ' are defined by:

$$T > T_c : \chi(T, H = 0) \propto (T - T_c)^{-\gamma} \tag{5.4}$$

$$T < T_c : \chi(T, H = 0) \propto (T_c - T)^{-\gamma'} \tag{5.5}$$

Experiments suggest that in general $\gamma = \gamma'$. Our example is a magnetic system, but can be generalized to an arbitrary phase transition by replacing M with the order parameter for that transition and H by the corresponding force.

The specific heat (the heat capacity per unit volume) behaves in a special way:

$$T > T_c : C(T, H = 0) \propto (T - T_c)^{-\alpha} \tag{5.6}$$

$$T < T_c : C(T, H = 0) \propto (T_c - T)^{-\alpha'} \tag{5.7}$$

Experiment shows again that in general $\alpha = \alpha'$.

*Are these critical exponents **independent** variables?*

CORRELATION LENGTH.

In the previous chapter we have seen that including fluctuations in a description of a material leads to the idea of a correlation length ξ. This correlation length ξ is associated with a parameter ν:

$$T > T_c : \xi(T) \propto (T - T_c)^{-\nu} \tag{5.8}$$

$$T < T_c : \xi(T) \propto (T_c - T)^{-\nu'} \tag{5.9}$$

Again, we will usually find $\nu = \nu'$.

UNIVERSALITY.

The powers in all these relations are called critical exponents. It turns out that critical exponents are a unique characterization of phase transitions. If two seemingly different phase transitions have exactly the same critical exponents, the underlying physics must be similar. This is an example of universality. We use the values of the critical exponents to classify second order phase transitions, and we find that there are only a few groups. For example, the critical exponents in the magnetic phase transitions for iron and nickel are the same, which tells us that the same physics is at work. Of course, the critical temperature has a very different value, which simply reflects the fact that we are dealing with different materials. But if we find an other magnetic phase transition with different values of the critical exponents, we know that something different is going on, and that we will need different models to describe this new material.

Critical exponents for the liquid to gas transition.

Critical exponents can also be defined for a liquid to gas phase transition. The intensive parameters controlling the phase transition are pressure and temperature and T_c in the formulas above must be set equal to the temperature at the critical point. The coexistence curve $p_{co}(T)$ has the same role as the line $H(T) = 0$ in the magnetic phase transition, it represents a discontinuity. If we expose a ferromagnetic material to a magnetic field, cool it below the critical temperature, and then reduce the field to zero, the final result will de different for positive or negative fields. The line $(T, H = 0)$ from $T = 0$ to $T = T_c$ represents all points in phase space where this discontinuity occurs. In the same way, if we apply pressure to a gas/liquid, cool it below the critical temperature, and then have the pressure approach $p_{co}(T)$, we observe a discontinuity depending on the path in (p,T) space.

Superconductivity.

A more complex example of a second order phase transition is found in superconductivity. In this case the order parameter is the pseudo wave function $\psi(\vec{r})$ representing the super-conducting electrons. The density $|\psi(\vec{r})|^2$ represents the density of super-conducting electrons at point $\vec{r}$. There is a bit of a problem, since we need to know what the force corresponding to the order parameter is. If we use the square of the pseudo wave function, the generalized force obviously is some sort of chemical potential. It is not easy to find out which generalized force corresponds to the pseudo wave functions itself.

Landau model for superconductivity.

Deep inside a superconductor we assume that we can describe the free energy by

$$f(T; \psi) = f_{normal}(T) + \frac{1}{2}\alpha(T)|\psi(\vec{r})|^2 + \frac{1}{4}\beta(T)|\psi(\vec{r})|^4 \qquad (5.10)$$

and in order to model a second order phase transition we assume that $\alpha(T)$ changes sign at T_c and that $\beta(T) > 0$. Therefore we find below T_c that

$$|\psi(\vec{r})|^2 = -\frac{\alpha(T)}{\beta(T)} \qquad (5.11)$$

The difference in free energy between the two states, the normal state and the super-conducting state, is given by

$$f_{sc} - f_{normal} = -\frac{1}{4}\frac{\alpha^2}{\beta} \qquad (5.12)$$

and this energy can be related to the critical field $H_c(T)$ for a type I supercon-
ductor by setting this equal to the energy density, because a type I supercon-
ductor expels all magnetic fields. This gives

$$-\frac{H_c^2(T)}{8\pi} = -\frac{1}{4}\frac{\alpha^2}{\beta} \tag{5.13}$$

Why is this a good assumption?

Next we assume that in the description of α near T_c we only need to include
the linear terms, and hence that $\alpha(T) \propto (T - T_c)$. This gives

$$H_c(T) \propto T_c - T \tag{5.14}$$

which is indeed observed, and

$$|\psi(\vec{r})|^2 \propto T_c - T \tag{5.15}$$

which agrees with the older theory due to London.

FLUCTUATIONS.

Our next task is to include fluctuations in this model. The pseudo wave
function is described by a Schrödinger type of equation, and the corresponding
energy, including a magnetic field (using a vector potential $\vec{A}$) is

$$\frac{1}{2m^*}\left|\left(\frac{\hbar}{\imath}\vec{\nabla} - \frac{e^*}{c}\vec{A}\right)\psi\right|^2 \tag{5.16}$$

where m^* is the mass of the super-conducting species (i.e. a Cooper pair) and
e^* its charge. Even though deep inside the superconductor there is no magnetic
field, we need to include the vector potential in order to describe the interface
between the super-conducting and normal regions. This form of the extra free
energy term is very similar to the Ginzburg term discussed before.

Next, we separate the pseudo wave function into a magnitude and phase by
$\psi = |\psi|e^{\imath\phi}$ which leads to the following form of the energy term:

$$\frac{1}{2m^*}\left(\hbar^2\left(\vec{\nabla}|\psi|\right)^2 + \left(\hbar\vec{\nabla}\phi - \frac{e^*}{c}\vec{A}\right)^2|\psi|^2\right) \tag{5.17}$$

where all cross terms disappear since they are purely imaginary. The first term
depends only on the magnitude of the order parameter and is the same as the
term introduced in the last chapter. The second term reflects a gauge invariance,
and is a pure quantum mechanical effect.

PHASE OF THE PSEUDO WAVE FUNCTION.

If there are no external fields and $\vec{A} = 0$ the minimum in the free energy occurs when $\vec{\nabla}\phi = 0$ or $\phi = constant$, which means that ϕ is not important in this case. In general we have

$$\hbar\vec{\nabla}\phi = \frac{e^*}{c}\vec{A} \tag{5.18}$$

relating the phase and the vector potential.

CORRELATION LENGTH.

The results from the previous chapter allow us to say that the correlation length in this case is given by

$$\xi(T) = \sqrt{\frac{\hbar^2}{2m^*\alpha(T)}} \tag{5.19}$$

which diverges in the usual way near the critical temperature. The interpretation of this correlation length is simple. If we have an interface between a normal state and a super-conducting state, the domain wall separating these two states is of thickness ξ.

Another important length scale is the length $\lambda_L(T)$ over which a magnetic field dies out inside the superconductor due to the flux expulsion. A comparison of the values of $\lambda_L(T)$ and ξ allows us to decide if a superconductor is of type I or type II.

5.2 Mean field theory.

MEANING OF DIFFERENT PARAMETERS.

In the study of phase transitions we distinguish two types of parameters that characterize a transition. When we consider the terms in the work done on a sample, we have products like HM and pV. We also have heat exchange, corresponding to a term TS. A phase transition is first characterized by a critical value in the temperature, T_c, below which temperature the sample is ordered when other fields are not present, i.e. H=0, p=0, etc. But we need also consider the roles of the other external controls we have on the sample. For example, in a magnetic phase transition we also have a critical value of the field, H_c, which is often equal to zero. The critical point in the (T, H) plane is (T_c, H_c). If we reduce the temperature through the critical value with a field slightly higher than H_c we end up with one type of magnetization, and if we lower the temperature with a field slightly below H_c we obtain the opposite magnetization.

If we also allow pressure to play a role, we find that the critical point is given by three parameters, T_c, H_c, and p_c.

The position of the critical point depends on the strength of the interactions, and on the type of interactions. Even though iron and nickel are both ferromagnetic materials, the critical temperatures are very different. In terms of models, they have different exchange interactions.

Phase transitions are also characterized by critical exponents, as defined earlier. As it turns out, these critical exponents do not depend on the strength of the interactions, they only depend on the **form of the Hamiltonian**, or on the nature of the interactions. Therefore, systems with similar values of the critical exponents are similar in nature, or have similar physics. Critical exponents are a tool to classify different types of phase transitions, or to sort them into different universality classes. In the following we discuss an important example.

What does "form of the Hamiltonian" mean?

LANDAU AND MEAN FIELD.

The second order phase transition we have studied as an example in Landau theory has a special meaning. If we ignore fluctuations, and only include the lowest order terms, the external magnetic field is given by (with $T < T_c$)

$$H = \left(\frac{\partial f}{\partial m}\right)_T = b(T)m + cm^3 \tag{5.20}$$

which can be written as

$$b_0 Tm = H + m(b_0 T_c - cm^2) \tag{5.21}$$

and near the critical temperature this is approximately $b_0 Tm = H + mb_0 T_c$. In free space the magnetization and field are proportional. In a paramagnetic substance the relation between the magnetization and the magnetic field is given by Curie's law $m = \alpha\frac{H}{T}$. The equation 5.21 looks like Curie's law, except that the magnetic field is modified. Because a magnetization is present there is an additional effective magnetic field $H' = m(b_0 T_c - cm^2)$. This can be interpreted as follows. Because a magnetization is already present, each sub-system in our large system experiences an additional magnetic field which is simply related to the average magnetization in the system. This is called a mean field approach. It ignores the effect that there are fluctuations in the magnetization.

CRITICAL EXPONENTS IN MEAN FIELD.

The critical exponents for Landau's theory in this mean field approach follow immediately from the equations we derived before:

$$m \propto (T_c - T)^{\frac{1}{2}} \Rightarrow \beta = \frac{1}{2} \tag{5.22}$$

$$\chi^{-1}(T, H) = \left(\frac{\partial^2 f}{\partial m^2}\right)_T \propto |T - T_c| \Rightarrow \gamma = \gamma' = 1 \tag{5.23}$$

$$T = T_c, f \propto m^4 \Rightarrow \delta = 3 \tag{5.24}$$

The value of α cannot be determined, since we did not specify a(T). Since a(T) is actually independent of the phase transition, it is reasonable to assume that it does not diverge at T_c, and in that case we find

$$\alpha = \alpha' = 0 \tag{5.25}$$

Any phase transition with the same critical exponents as we listed here has the same physics incorporated. Any model with these critical exponents is therefore essentially a mean field model!

EXAMPLE VALUES.

The following table gives some examples of measured values of critical exponents and theoretical results:

type	system	T_c	α	β	γ	δ
ferromagnetic	Ni	632	-0.10	0.33	1.32	4.2
	Fe	1044	-0.12	0.34	1.33	
anti-ferromagnetic	$RbMnF_3$	83	-0.14	0.32	1.40	
liquid-gas	Co_2	304	0.12	0.34	1.20	4.2
	Xe	290	0.08	0.34	1.20	4.4
ordered alloy	$CoZn$	739		0.31	1.25	
mean field			0	0.5	1.0	3.0
Ising, d=2			0	0.125	1.75	15
Ising, d=3			0.12	0.31	1.25	5.0
Heisenberg			-0.14	0.38	1.38	

If mean field theory would be valid for all systems, all systems would have the same values for the critical exponents. In some sense this is obeyed. They are indeed quite close, but distinct from mean field. The fact that the critical exponents do not vary wildly is due to the fact that in many systems mean field theory is a good first approximation.

A very different set of values is obtained in the 2 dimensional Ising model. This shows the importance of the dimensionality of the system, and hence we expect big differences between the properties of thin films and bulk solids, which is indeed observed. The difference between the 3 dimensional Ising model and

the Heisenberg model is not very large, but large enough that experiments can distinguish between the validity of the two.

In experimental situations we often study thin films, and the question always arises if these films are two or three dimensional. The answer to this question is easy. One length scale of importance is the thickness of the film, T_{film}. The other quantity of interest is the correlation length $\xi(T)$. If we have $\xi(T) < T_{film}$, even in the direction perpendicular to the film we have many domains, or regions of different organized behavior, and the film is three dimensional. On the other hand, if $\xi(T) > T_{film}$ the film is always coherent over the whole thickness, and we have a two dimensional system. In the thermodynamic limit we assume that the extend of the film in the plane is infinite, and in that direction we always have a correlation length smaller than the dimensions of the film. **This argument therefore shows that a thin film near the critical temperature always behaves as a two dimensional system.** This situation is more complicated when we have two different types of correlation length to consider, in that case we have to ask the question large or small for each of those lengths.

What is near?

EXAMPLE VAN DER WAALS.

In Chapter 3 we studied a model of the liquid to gas phase transition developed by van der Waals. This model was very instructive, and explained many characteristics of the phase transition. It essentially captured the behavior using two parameters, a and b. Based on the values for a and b we found the critical temperature and pressure. Hence, it is also possible to use the critical temperature and pressure as parameters describing the phase transition. There are no parameters left, and therefore the critical exponents should all be determined by the form of the equation!

PARAMETER FREE VAN DER WAALS EQUATION.

Once the critical temperature and pressure are known, the van der Waals equation should be unique. This leads us to the introduction of the following relative variables:

$$\theta = \frac{T - T_c}{T_c} \qquad (5.26)$$

$$\pi = \frac{p - p_c}{p_c} \qquad (5.27)$$

$$\upsilon = \frac{V - V_c}{V_c} \qquad (5.28)$$

and in terms of these variables the van der Waals equation is

$$\left[(1 + \pi) + \frac{3}{(1 + v)^2}\right] [3(1 + v) - 1] = 8(1 + \theta) \tag{5.29}$$

which is indeed parameter-free. Since we are interested in the behavior near the critical point, where all scaled parameter values are small, we rewrite this equation as follows by multiplying by $(1 + v)^2$:

$$\left[(1 + \pi)(1 + v)^2 + 3\right] [2 + 3v] = 8(1 + \theta)(1 + v)^2 \tag{5.30}$$

or

$$\left[4 + 2v + v^2 + \pi + 2\pi v + \pi v^2\right] [2 + 3v] = 8(1 + \theta)(1 + 2v + v^2) \tag{5.31}$$

or

$$8 + 16v + 8v^2 + 2\pi + 7\pi v + 8\pi v^2 + 3v^3 + 3\pi v^3 = 8 + 16v + 8v^2 + 8\theta + 16\theta v + 8\theta v^2 \tag{5.32}$$

or

$$\pi \left(2 + 7v + 8v^2 + 3v^3\right) + 3v^3 = \theta \left(8 + 16v + 8v^2\right) \tag{5.33}$$

which is a good start for the derivation of the values of the critical exponents.

REDUCED PRESSURE EXPANSION.

In order to analyze the behavior near the critical point, we expand the reduced pressure as a function of reduced temperature and reduced volume near the critical point and find that:

$$\pi \approx 4\theta - 6\theta v + 9\theta v^2 - \frac{3}{2}v^3 \tag{5.34}$$

where in the third order volume term the small θ term is ignored, and the higher order volume terms are ignored. This equation gives a good and valid description of the behavior near the critical point.

The partial derivative of the pressure versus volume is:

$$\left(\frac{\partial \pi}{\partial v}\right)_\theta \approx -6\theta + 18\theta v - \frac{9}{2}v^2 \tag{5.35}$$

and equating this to zero has solutions if $18^2\theta^2 \geq 108\theta$ or $\theta \leq 0$ for the solution close to the critical point, as expected.

ORDER PARAMETER.

For $\theta \leq 0$ and close to zero we can find the volume of the liquid and the gas phase from the equations:

$$\pi(v_l) = \pi(v_g) \qquad (5.36)$$

and

$$0 = \int_{v_l}^{v_g} v d\pi \qquad (5.37)$$

The first equation is equivalent to:

$$-6\theta v_l + 9\theta v_l^2 - \frac{3}{2}v_l^3 = -6\theta v_g + 9\theta v_g^2 - \frac{3}{2}v_g^3 \qquad (5.38)$$

while the last equation is equivalent to:

$$0 = \int_{v_l}^{v_g} v \left(\frac{\partial \pi}{\partial v} \right)_\theta dv \qquad (5.39)$$

or

$$0 = \int_{v_l}^{v_g} v(-6\theta + 18\theta v - \frac{9}{2}v^2)dv \qquad (5.40)$$

or

$$-3\theta v_l^2 + 6\theta v_l^3 - \frac{9}{8}v_l^4 = -3\theta v_g^2 + 6\theta v_g^3 - \frac{9}{8}v_g^4 \qquad (5.41)$$

Close to the critical point the middle term in each equation can be ignored, because it is small compared to the first term. We cannot ignore the third term, since it does not contain the temperature, and we do not yet know the relative scaling of all quantities. As a consequence, we find that we need to solve:

$$4\theta v_l + v_l^3 = 4\theta v_g + v_g^3 \qquad (5.42)$$

and

$$8\theta v_l^2 + 3v_l^4 = 8\theta v_g^2 + 3v_g^4 \qquad (5.43)$$

How to solve these equations? First of all, note that we expect $v_l < 0 < v_g$. The two previous equations can be rewritten in the form:

$$4\theta(v_l - v_g) = v_g^3 - v_l^3 \qquad (5.44)$$

and

$$8\theta(v_l^2 - v_g^2) = 3(v_g^4 - v_l^4) \qquad (5.45)$$

The first has solutions $v_l = v_g$, which is not physical because $v_l < 0 < v_g$. Hence we are left with

$$-4\theta = v_g^2 + v_l v_g v_l^2 \tag{5.46}$$

The second equation has solutions

$$v_l^2 = v_g^2 \tag{5.47}$$

or $v_l = -v_g$. Together with the first equation this gives the solutions according to

$$v_g = -v_l = 2\sqrt{|\theta|} \tag{5.48}$$

which are only valid for $\theta < 0$, as expected. The other solution of the second equation is

$$8\theta = 3(v_g^2 + v_l^2) \tag{5.49}$$

which cannot be right since it would imply $\theta > 0$.

The order parameter Δv is defined as the difference between the volumes, and we have

$$\Delta v = 4\sqrt{|\theta|} \tag{5.50}$$

along the coexistence curve given by

$$\pi_{coex} = 4\theta \tag{5.51}$$

HEAT CAPACITY.

We have seen in chapter 3 that the heat capacity as a function of temperature always shows a finite jump. There is no divergence, but the values of the heat capacity are not the same coming from below or above the critical temperature. This is simply related to the fact that we have a continuous path from the gas to the liquid state following a van der Waals curve. The Gibbs free energy of the gas and liquid are the same at the coexistence curve, but the slope as a function of temperature changes.

The Gibbs free energy follows from

$$g = g_0(\theta) + \int_0^v v d\pi = g_0(\theta) - 3\theta v^2 + 6\theta v^3 - \frac{9}{8}v^4 \tag{5.52}$$

which leads to the entropy

$$-s = \left(\frac{\partial g}{\partial \theta}\right)_\pi = g_0'(\theta) - 3v^2 + 6v^3 + \left(-6\theta v + 18\theta v^2 - \frac{9}{2}v^3\right)\left(\frac{\partial v}{\partial \theta}\right)_\pi \tag{5.53}$$

and a specific heat

$$-c = \theta \left(\frac{\partial s}{\partial \theta} \right)_{\pi} = \theta g_0''(\theta) + 2\theta \left(-6v + 18v^2 \right) \left(\frac{\partial v}{\partial \theta} \right)_{\pi} +$$

$$\theta \left(-6\theta + 36\theta v - \frac{27}{2} v^2 \right) \left(\frac{\partial v}{\partial \theta} \right)_{\pi}^2 + \theta \left(-6\theta v + 18\theta v^2 - \frac{9}{2} v^3 \right) \left(\frac{\partial^2 v}{\partial \theta^2} \right)_{\pi} \quad (5.54)$$

which does not diverge, but is discontinuous (i.e. does not have the same value for v_l and v_g. Near the transition we can therefore model the heat capacity by

$$\theta > 0 : C(\theta, \pi = \pi_{coex}) \propto \theta^{-\alpha} \quad (5.55)$$

$$\theta < 0 : C(\theta, \pi = \pi_{coex}) \propto |\theta|^{-\alpha'} \quad (5.56)$$

and the only way to get a discontinuity is to have

$$\alpha = \alpha' = 0 \quad (5.57)$$

ORDER PARAMETER.

From equation 5.50 gives immediately that

$$\beta = \frac{1}{2} \quad (5.58)$$

ORDER PARAMETER VERSUS FIELD.

This response function follows from (leaving out a factor $\frac{V p_c}{V_c}$, which does not change the value of the critical exponent):

$$-\kappa^{-1} = \left(\frac{\partial \pi}{\partial v} \right)_{\theta} = -6\theta + 18\theta v - \frac{9}{2} v^2 \quad (5.59)$$

which we need to follow along $\pi_{coex} = 4\theta$ or

$$0 = -6\theta v + 9\theta v^2 - \frac{3}{2} v^3 \quad (5.60)$$

which can be used (after dividing by v) to eliminate the last term, and we get

$$\theta < 0 : \kappa^{-1} = -12\theta + 9\theta v \quad (5.61)$$

in which only the first term is important near the critical point. Similarly, above the critical temperature we follow the constant volume curve and find:

$$\theta > 0 : \kappa^{-1} = +6\theta \quad (5.62)$$

which leads immediately to

$$\gamma = \gamma' = 1 \tag{5.63}$$

VOLUME VERSUS PRESSURE AT THE CRITICAL TEMPERATURE.

The equation here is simple, we have

$$\pi = -\frac{3}{2}v^3 \tag{5.64}$$

which shows immediately that

$$\delta = 3 \tag{5.65}$$

VAN DER WAALS IS MEAN FIELD.

We have found that the critical exponents in a van der Waals model of a phase transition are the same as the mean field exponents. Therefore, the van der Waals model is a mean field model. This can be explained easily in a microscopic model, where the parameters a and b only describe the average interaction between molecules, or the interaction between one molecule and its average (mean) environment. The van der Waals equation of state is no exception. In fact, any analytic equation of state model of a phase transition gives the same mean field exponents, since in relative units the form of the equation near the critical point is always like equation 5.34!

5.3   Model free energy near a critical point.

FLUCTUATIONS.

By now it will be clear that any realistic description of a phase transition near a critical point will have to include the effects of fluctuations. Without that, we only have analytical theories with discontinuities at the transition, which lead to mean field values of the critical exponents. In order to illustrate the approach to the problem of including fluctuations, we will again study a magnetic phase transition, but the procedure can be generalized to arbitrary systems.

SCALED VARIABLES.

The important variables which we can use to change the state of our model system are the temperature T and the magnetic field H. The critical point is

given by the values T_c and $H_c = 0$. In order to focus on the behavior near the critical point we used scaled values of these variables:

$$\theta = \frac{T - T_c}{T_c} \tag{5.66}$$

and

$$h = H \tag{5.67}$$

where the scaling in the last case is simple, since we cannot divide by zero.

MODEL ENERGY.

The important free energy in this case is a analogue to the Gibbs free energy (the magnetic Gibbs free energy) defined by

$$g(\theta, h) = \frac{1}{N}(U - TS - MH) \tag{5.68}$$

where we also divided by the total amount of material to get an energy density. One important contribution to this free energy is the normal equilibrium thermodynamical form we have discussed before. This term only leads to continuous behavior, without any divergent behavior in the energy. The previous section showed that the free energy for a van der Waals model is smooth, for example. This term is the background energy. The free energy, however, also contains a term describing the fluctuations in the system. This is the term we do not know how to write down formally, but we can separate the effects:

$$g(\theta, h) = g_{background}(\theta, h) + g_{fluctuations}(\theta, h) \tag{5.69}$$

ANALYSIS OF FLUCTUATION TERM.

When we get closer to the critical temperature, the effect of fluctuations will dominate the behavior of the system. These fluctuations will cause all kinds of divergencies in the response functions. We therefore assume that near the critical point only the second term in the last equation is important. The analysis of critical exponents is therefore determined by the second term, and from now on we ignore the first term and omit the subscript fluctuations. The main question is, what kind of general statements can we make about this energy term!

SCALING.

Near a critical point the correlation length becomes very large. Any other length scale we have in the system is not important anymore, and the correlation length determines the behavior of the system. Suppose we have a picture of a

system close to a critical point. We see bubbles of one phase in another, and the average size of these bubbles is related to the correlation length. If we change the values of the temperature or field slightly, we obtain a different picture with a different average size of the bubbles. If we have an absolute measure of the length scale we can identify these pictures. But imagine that both pictures are scaled and that one unit of length in each picture corresponds to the appropriate correlation length. In this case the average size of the bubbles will be the same in both pictures. Can we still identify the pictures? Can we tell them apart? The experimental answer seems to be no. Therefore, the free energy due to the fluctuations in both cases must be related, and the density is changed by simply accounting for the extra amount of material in a scaled unit volume. Mathematically this is expressed by saying that the free energy g (due to the fluctuations) near the critical point should be a homogeneous function of its variables.

HOMOGENEOUS FUNCTIONS.

Homogeneous functions are easiest to discuss when only one variable is involved. By definition, a function f(x) is called homogeneous if

$$f(\lambda x) = S(\lambda)f(x) \tag{5.70}$$

where S is called a scaling function. This relation has to hold for all values of λ and x. In this simple case it is easy to derive what the possible homogeneous functions are. When we apply to successive transformations we get

$$f((\mu\lambda)x) = S(\mu\lambda)f(x) \tag{5.71}$$

but also

$$f((\mu\lambda)x) = f(\mu(\lambda x)) = S(\mu)S(\lambda)f(x) \tag{5.72}$$

or

$$S(\mu\lambda) = S(\mu)S(\lambda) \tag{5.73}$$

for all values of λ and μ. If we now take the derivative with respect to λ we obtain

$$S'(\mu\lambda)\mu = S(\mu)S'(\lambda) \tag{5.74}$$

and similarly for μ:

$$S'(\mu\lambda)\lambda = S'(\mu)S(\lambda) \tag{5.75}$$

from which follows:

$$S(\mu)S'(\lambda)\lambda = \mu S'(\mu)S(\lambda) \tag{5.76}$$

or

$$\frac{S'(\lambda)\lambda}{S(\lambda)} = \frac{\mu S'(\mu)}{S(\mu)} \tag{5.77}$$

which means that

$$\frac{S'(\lambda)\lambda}{S(\lambda)} = p \tag{5.78}$$

where p is a constant. Since S(1)=1 we can solve this immediately and we get

$$S(\lambda) = \lambda^p \tag{5.79}$$

FORM OF THE SCALING FUNCTIONS.

We arrive at the important conclusion that scaling functions are simple powers of the variable, where the constant p can take any real value. In equation 5.70 we can take x=1 and find

$$f(\lambda) = \lambda^p f(1) \tag{5.80}$$

which shows that the homogeneous functions of one variable are simple powers. For example, for the volume V of a cube with side a we find that $V(\lambda a) = \lambda^3 V(a)$.

HOMOGENEOUS FUNCTION IN MANY VARIABLES.

Homogeneous functions of many variables are defined in a similar manner, where we already include the fact that the scaling functions are powers. The only change we make is where we put the scaling function, and in this case it is easier to have the simple multiplier variable λ in front of the function:

$$f(\lambda^p x, \lambda^q y) = \lambda f(x, y) \tag{5.81}$$

Since the powers p and q can take any real value, we need to restrict ourselves to positive values of lambda only.

SCALING APPLIED TO THE FREE ENERGY.

The basic idea that the correlation length is the only important length scale near the critical point translates in the following statement for the energy density. Near the critical point $\theta = 0$, $h = 0$ we have

$$g(\lambda^p \theta, \lambda^q h) = \lambda g(\theta, h) \tag{5.82}$$

5.4   Consequences of scaling.

The scaling relation in equation 5.82 has some very important consequences. For example, if we calculate the magnetization $m = \left(\frac{\partial g}{\partial h}\right)_\theta$ we find that

$$\lambda^q m(\lambda^p \theta, \lambda^q h) = \lambda m(\theta, h) \tag{5.83}$$

and therefore if we set $\theta = 1$ and $h = 0$ we obtain

$$m(\lambda^p, 0) = \lambda^{1-q} m(1, 0) \tag{5.84}$$

or with $t = \lambda^p$

$$m(t, 0) = t^{\frac{1-q}{p}} m(1, 0) \tag{5.85}$$

Since $m(1, 0) = 0$ we find therefore that $m(t, 0) = 0$ for all values of t and that there is no magnetization. But here we have to be careful. Since $\lambda > 0$ this only holds for $t > 0$, and now our conclusion is indeed correct. Scaling tells us that if the magnetization is zero at one point above the critical temperature, it is zero everywhere above the critical temperature.

RELATION TO CRITICAL EXPONENT β.

In order to discuss the behavior below the critical temperature we need to start with $\theta = -1$. This gives:

$$m(-\lambda^p, 0) = \lambda^{1-q} m(-1, 0) \tag{5.86}$$

or with $t = -\lambda^p$

$$m(t, 0) = (-t)^{\frac{1-q}{p}} m(-1, 0) \tag{5.87}$$

In this case $m(-1, 0)$ is not zero and we find that the magnetization near the critical temperature follows a simple power law as a function of the reduced temperature, as expected. A comparison with the definition of the critical exponent β gives

$$\beta = \frac{1-q}{p} \tag{5.88}$$

and hence the value of the critical exponent follows immediately from the scaling parameters p and q in the energy! This is true for all critical exponents! Since we only have two independent parameters in the energy scaling, we see that only two values of the critical exponents are independent, and that the others should de dependent!

CRITICAL EXPONENT δ.

From equation 5.83 we see immediately that

$$\lambda^q m(0, \lambda^q h) = \lambda m(0, h) \tag{5.89}$$

and with $h = 1$ we obtain

$$m(0, \lambda^q) = \lambda^{1-q} m(0, 1) \tag{5.90}$$

or by defining $|H| = \lambda^q$ we find

$$m(0, |H|) = |H|^{\frac{1-q}{q}} m(0, 1) \tag{5.91}$$

or

$$\delta = \frac{q}{1 - q} \tag{5.92}$$

CRITICAL EXPONENT γ.

The susceptibility follows from $\chi = \left(\frac{\partial m}{\partial h}\right)_\theta$ and the scaling relation 5.83 leads to

$$\lambda^{2q} \chi(\lambda^p \theta, \lambda^q h) = \lambda \chi(\theta, h) \tag{5.93}$$

In this equation we use again $h = 0$, and again distinguish between temperatures above and below the critical temperature. We find

$$t > 0 : \chi(t, 0) = t^{\frac{1-2q}{p}} \chi(1, 0) \tag{5.94}$$

and

$$t < 0 : \chi(t, 0) = (-t)^{\frac{1-2q}{p}} \chi(-1, 0) \tag{5.95}$$

which shows that the critical exponents are indeed the same above and below the critical point:

$$\gamma = \gamma' = \frac{2q - 1}{p} \tag{5.96}$$

but that the pre-factors are different.

SPECIFIC HEAT.

The specific heat follows from $c_h = -T \left(\frac{\partial^2 g}{\partial \theta^2}\right)_h$ where the temperature in front is the real temperature, not the scaled one. This gives

$$\lambda^{2p} c_h(\lambda^p \theta, \lambda^q h) = \lambda c_h(\theta, h) \tag{5.97}$$

which then leads to

$$t > 0 : c_h(t, 0) = t^{\frac{1-2p}{p}} c_h(1, 0) \tag{5.98}$$

and

$$t < 0 : c_h(t,0) = (-t)^{\frac{1-2p}{p}} c_h(-1,0) \tag{5.99}$$

which shows again that the critical exponents are indeed the same above and below the critical point:

$$\alpha = \alpha' = \frac{2p - 1}{p} \tag{5.100}$$

and again that the pre-factors are different.

SCALING RELATIONS.

Using the expressions for the critical exponents it is possible to derive relations between these exponents by eliminating the variables p and q. For example, we have

$$(\delta + 1)\beta = (\frac{q}{1 - q} + 1)\frac{1 - q}{p} = \frac{1}{p} = 2 - \alpha \tag{5.101}$$

and if we check this for the mean field exponents we see that there indeed $(\delta + 1)\beta = 4 \times \frac{1}{2} = 2 - \alpha$ indeed.

Similarly we find that

$$(\delta - 1)\beta = (\frac{q}{1 - q} - 1)\frac{1 - q}{p} = \frac{2q - 1}{p} = \gamma \tag{5.102}$$

which was already discovered by Widom before the formulation of scaling theory. It is easy to check that the mean field exponents satisfy this equality. Another equation, named after Rushbrooke, is also easily derived:

$$\alpha + 2\beta + \gamma = 2 \tag{5.103}$$

Note that we can work backwards and find that in mean field theory we have

$$p_{MF} = \frac{1}{2} \tag{5.104}$$

and

$$q_{MF} = \frac{3}{4} \tag{5.105}$$

A final note, in this type of scaling we always find that $\alpha = \alpha'$ and $\gamma = \gamma'$, because we assume that the scaling is the same below and above the critical temperature.

COMPARISON WITH EXPERIMENT.

We can look at the experimental data presented before, and construct the following table:

type	$1 - \frac{\alpha+\gamma}{2}$	β	$1 + \frac{\gamma}{\beta}$	δ
ferromagnetic Ni	0.39	0.33	5.0	4.2
ferromagnetic Fe	0.39	0.34		
anti-ferromagnetic $RbMnF_3$	0.37	0.32		
liquid-gas Co_2	0.34	0.34	4.5	4.2
liquid-gas Xe	0.36	0.34	4.5	4.4
mean field	0.5	0.5	3.0	3.0
Ising, d=2	0.125	0.125	15	15
Ising, d=3	0.31	0.31	5.0	5.0
Heisenberg	0.38	0.38		

which is reasonable. One has to keep in mind that critical exponents are very difficult to measure, and that the error bars are large. If we take that into account, we conclude that the experimental results do not contradict scaling.

EQUALITIES OR INEQUALITIES?

The basis for the equalities can be discussed in a completely different manner. In chapter 2 we derived inequalities related to thermodynamic stability. For example, we found that

$$C_H - C_M \geq \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T} \right)_H^2 \tag{5.106}$$

and since $C_M > 0$ we can drop the term C_M in the left hand side. Near the critical point we have $C_H = c_1 |\theta|^{-\alpha}$, $\chi_T = c_2 |\theta|^{-\gamma}$, and $\left(\frac{\partial M}{\partial T} \right)_H = c_3 |\theta|^{\beta-1}$, which gives

$$c_1 |\theta|^{-\alpha} \geq \frac{Tc_3^2}{c_2} |\theta|^{2\beta+\gamma-2} \tag{5.107}$$

and this should be true even in the limit $\theta \to 0$, which leads to

$$-\alpha \leq 2\beta + \gamma - 2 \tag{5.108}$$

or

$$\alpha + 2\beta + \gamma \geq 2 \tag{5.109}$$

as originally discovered by Rushbrooke.

In a similar manner one can derive

$$\gamma \geq \beta(\delta - 1) \tag{5.110}$$

which was originally shown by Widom.

The derivation above is based on equilibrium thermodynamics. In scaling theory we describe a non-equilibrium state with fluctuations. But if we think of a given state with two phases present, where one phase is meta-stable, we

can still apply the same kind of analysis to the meta-stable state, since it still corresponds to a minimum in the free energy.

Explain this carefully.

One can therefore argue that the inequality 5.109 should also hold for the singular part of the free energy. Scaling theory confirms that, but is also much more restrictive, because it forces the inequality to be an equality.

PAIR CORRELATION FUNCTION.

In the previous chapter we discussed how the effects of a small perturbation are felt further away in the system. In Ginzburg-Landau theory it was possible to calculate the change in magnetization density caused by a perturbation at the origin. The function in equation 4.56 is an example of a pair correlation function, i.e. a function describing how the magnetization at two different sites is related. The formal definition of the pair correlation function Γ is

$$\Gamma(T, \vec{r}, \vec{r}') = \langle (m(\vec{r}) - m_0)(m(\vec{r}') - m_0) \rangle \qquad (5.111)$$

where m_0 is the average value of the magnetization. The pair correlation function will also depend on the temperature, of course, and on other thermodynamic variables. In a homogeneous system the pair correlation function will only depend on the distance $|\vec{r} - \vec{r}'|$ between the points. In Ginzburg-Landau theory we found that the pair correlation is proportional to the function calculated in equation 4.56, since this function gives us the extra magnetization when the origin has a large magnetization (driven by a delta function applied field). Therefore, in that case:

$$\Gamma(T, r) \propto \frac{1}{r} e^{-\frac{r}{\xi}} \qquad (5.112)$$

TWO CRITICAL EXPONENTS.

The critical exponents ν and ν' describe the behavior of the correlation length ξ close to the critical temperature:

$$T > T_c : \xi(T) \propto (T - T_c)^{-\nu} \qquad (5.113)$$

$$T < T_c : \xi(T) \propto (T_c - T)^{-\nu'} \qquad (5.114)$$

and again we expect that scaling theory will give $\nu = \nu'$. Ginzburg-Landau theory gives $\nu = \nu' = \frac{1}{2}$. At the critical temperature the correlation length is

infinite, and the decay of the pair correlation function is given by the r dependence in front. Another critical exponent η is defined by:

$$\Gamma(T_c, r) \propto r^{2-d-\eta} \tag{5.115}$$

where d is the number of dimensions in the problem. Using the results of one of the problems in the previous chapter we see that $\eta = 0$ in all dimensions for mean field (Ginzburg-Landau) theory.

MOMENTUM SPACE.

In many cases we need the Fourier transform of the pair correlation function, and calculate

$$\int d^d r e^{i\vec{q}\cdot\vec{r}} \Gamma(T, r) \tag{5.116}$$

which for small q is proportional to $q^{\eta-2}$. This is often used as the definition for η, but is of course completely equivalent to our definition. Later we will discuss the exact definition of the structure factor, which is almost the same as the Fourier transform above. The difference is not essential for the current discussion.

RELATION TO THE SUSCEPTIBILITY.

Since the pair correlation function describes the average of fluctuations, we can use the techniques from the end of Chapter 2 to relate this to a response function, which in this case is the susceptibility. In order to find the susceptibility we need to take an average over all space, and hence we find that

$$\chi(T) \propto \int d^d r \Gamma(T, r) \tag{5.117}$$

or that the susceptibility is proportional to the Fourier transform of the pair correlation function at q=0.

Make sure that you understand the previous argument based on chapter 2.

5.5 Scaling of the pair correlation function.

We assume that near the critical point the correlation length is the only important length scale. As a result, the pair correlation function has to be a function of the ratio $\frac{r}{\xi}$ and we can write

$$\Gamma(T,r) = f(\frac{r}{\xi(T)})\xi^u(T) = \tilde{f}(\frac{r}{\xi(T)})r^u \qquad (5.118)$$

At the critical temperature the correlation length is infinite and therefore the second part of the equation above gives

$$\Gamma(T_c, r) = \tilde{f}(0)r^u \qquad (5.119)$$

which shows that $u = 2 - d - \eta$. The Fourier transform of the pair distribution function is

$$\int d^d r e^{\imath \vec{q} \cdot \vec{r}} f(\frac{r}{\xi(T)})\xi^u(T) \qquad (5.120)$$

which can be transformed using $\vec{r} = \xi(T)\vec{x}$ and $\vec{s} = \xi(T)\vec{q}$ into

$$\int d^d x e^{\imath \vec{s} \cdot \vec{x}} f(x)\xi^{u+d}(T) \qquad (5.121)$$

RELATION BETWEEN THE SUSCEPTIBILITY AND THE CORRELATION LENGTH.

Since the susceptibility is proportional to the q=0 component of the Fourier transform of the pair correlation function, we see that near the critical point the susceptibility is proportional to

$$\chi(T) \propto \xi^{u+d} = \xi^{2-\eta} \propto |T - T_c|^{-\nu(2-\eta)} \qquad (5.122)$$

which shows the important relation between the critical exponents:

$$\gamma = \nu(2 - \eta) \qquad (5.123)$$

5.6   Hyper-scaling.

Near the critical point the correlation length is the only important length scale, and this has one final consequence. The energy needed to create a fluctuation, independent of its size, will be a constant proportional to T_c. Later we can derive in a microscopic picture that it will be on the order of $k_B T_c$, but for our present discussion it is sufficient to assume that it is a constant per fluctuation. The volume of a fluctuation is proportional to ξ^d, and therefore we find that near the critical point the energy density scales like

$$g(\theta, h = 0) \propto \xi^{-d}(T) \qquad (5.124)$$

This assumption is called hyper-scaling. Near the critical point we therefore have

$$g(\theta, h = 0) \propto \theta^{\nu d} \qquad (5.125)$$

From the energy scaling relation 5.82 we find:

$$g(\lambda^p, 0) = \lambda g(1, 0) \tag{5.126}$$

and with $t = \lambda^p$ we get

$$g(t, 0) = t^{\frac{1}{p}} g(1, 0) \tag{5.127}$$

which shows that $\nu d = \frac{1}{p}$, or

$$d\nu = 2 - \alpha \tag{5.128}$$

which is NOT true for mean field theory combined with Ginzburg-Landau in three dimensions! The equation above would give $\nu = \frac{2}{3}$, while Ginzburg-Landau gives $\nu = \frac{1}{2}$. Therefore, Ginzburg-Landau theory does not obey hyper-scaling, and cannot be a complete theory at the transition. Note, however, that in **four dimensions** the equation above is obeyed. Perhaps something is special in four dimensions!

5.7 Validity of Ginzburg-Landau theory.

CRITERIUM FOR VALIDITY.

The theory put forward by Ginzburg and Landau is only a start for a description of the role of fluctuations. The critical exponents in this theory have the mean field values, and in real experiments those values are different. But it is still a fair question to ask when this theory is a good approximation. One criterium is the following. If we have fluctuations in a parameter, a theory that treats these as a perturbation needs to require that the fluctuations are small, or that

$$\Delta M \ll M \tag{5.129}$$

which, obviously, can only be applied for temperatures below the critical temperature. Note that we use the total magnetization in this formula. In Ginzburg-Landau we have

$$(\Delta M)^2 = \int d^3 r d^3 r' \langle (m(\vec{r}) - m_0)(m(\vec{r'}) - m_0) \rangle = V \int d^3 r \Gamma(T, r) \propto V \int d^3 r \frac{1}{r} e^{-\frac{r}{\xi}} \tag{5.130}$$

which leads to something like

$$(\Delta M)^2 = C_1 V \xi^2(T) \tag{5.131}$$

where C_1 is a constant independent of the temperature.

INEQUALITY FOR VALIDITY.

The total magnetization is simple, and we have $M = V m_0$. Therefore we have a condition of the form

$$C_1 V \xi^2(T) \ll m_0^2 V^2 \tag{5.132}$$

which is always obeyed in the thermodynamic limit $V \to \infty$. But that is not correct. **The thermodynamic limit should always be taken in the end**, and we first need to consider the behavior as a function of temperature. If we approach the critical points the correlation length becomes infinite, signalling that interchanging limits can be dangerous! Our criterium for validity should be that the fluctuations measured in a **relevant volume** must be small. Since the range of fluctuations are given by the correlation length, the obvious choice is to consider a volume determined by this correlation length! Therefore, we take $V = \xi^3(T)$.

Since the magnetization itself is determined by the critical exponent β we have the following inequality that gives a necessary criterium for the validity of Ginzburg-Landau theory:

$$C_1 \ll m_0^2 \xi \tag{5.133}$$

or

$$C_2 \ll \theta^{2\beta - \nu} \tag{5.134}$$

where all constants are lumped together in C_2. Using the appropriate values $\beta = \nu = \frac{1}{2}$ we get

$$|\theta| \gg C_2^2 \tag{5.135}$$

which shows that close to the critical point Ginzburg-Landau theory is not self-consistent, i.e. it predicts fluctuations which are so large that the basic assumptions of the theory are not valid anymore. Higher order gradients become important, and the series as an expansion in terms of gradients does not converge anymore.

NECESSARY OR SUFFICIENT.

Strictly speaking the criterium above is only a necessary criterium for the validity of the theory. In general, however, it will also be sufficient. If $|\theta| \gg C_2^2$ higher order gradients will be less and less important, and an expansion in terms of gradients is appropriate. But this is only a statement about very high orders. Ginzburg-Landau theory assumes that the lowest order gradient is the dominant term. This is not guaranteed, it could be possible that all the action is in the next term. Therefore, the condition we have derives is not sufficient in general. In practice, however, one will often find that the lowest order term is dominant,

and that the inequality derived above is also sufficient. An important exception does occur in all those cases where symmetry arguments make this term exactly zero! One should always keep that in mind.

Use of Ginzburg-Landau theory.

Nevertheless, the theory of Ginzburg and Landau is an improvement, and will give a better description of the system as long as the inequality above is obeyed. Hence we have the following picture. Far away from the critical point mean field theory is a good description of the system under consideration. When we get closer to the critical point, we can improve by including gradient terms in the expansion of the free energy. Very close to the critical point we need a different theory, however. In this chapter we have given a model of the free energy that describes the behavior at the critical point, but the critical exponents are parameters in that model (following from the values of p and q in equation 5.82). In order to derive the values of these critical exponents we need a different theory, however. This is usually done in statistical mechanics, where we include the microscopic nature of the material.

Range of validity.

The inequality $|\theta| \gg C_2^2$ gives us also an estimate of the range of validity. In order to calculate numerical values we do need to know the constant C_2, and hence we need the details of the model. It is possible that Ginzburg-Landau theory is valid essentially everywhere for our measurement (apart from giving the values of the critical exponents), but there are also situations where the excluded range is so large that this theory is never applicable.

Different dimensions.

We can also apply the previous argument for a system in d dimensions. In that case the pair correlation length is proportional to r^{2-d} (see problem in previous chapter), and the volume V is $V = \xi^d(T)$. This leads to

$$C_3 \ll m_0^2 \xi^{d-2} \tag{5.136}$$

or

$$C_4 \ll \theta^{2\beta-(d-2)\nu} \tag{5.137}$$

which is valid even at the critical point as long as $2\beta - (d-2)\nu < 0$ or

$$d > d^* = 2(1 + \frac{\beta}{\nu}) \tag{5.138}$$

Marginal dimension.

The constant d^* above is called the <u>marginal dimension</u>. In Ginzburg-Landau it has the value $d^* = 4$. The <u>condition $d > 4$ can be</u> interpreted as follows. If the number of dimensions is larger than four, mean filed theory will be valid (as long as the conditions described in the necessary versus sufficient paragraph are met). This is the basis for the famous epsilon expansion, where all quantities are expanded in a power series in terms of $d = d^* - \epsilon$ and the limit $d \rightarrow 3$ is taken to get results for the real world.

If we are exactly at the marginal dimension, mean field theory does not necessarily describe the physics of the problem, but the difference can only be in terms that diverge in a logarithmic fashion, i.e. slower than any arbitrary power of θ. Details can be quite messy in that case.

5.8   Scaling of transport properties.

Different basis for scaling.

We have introduced the scaling hypothesis by using the free energy. This seems an appropriate choice, since the free energy is the most important quantity from which all other thermodynamic variables can be derived. Using two basic scaling parameters, p and q, we were able to derive all critical exponents. The important observation is that there are only two independent variables, and any set of two exponents can be used as a basic set. Of course, as soon as we introduce more state variables, we obtain more possibilities. For example, if we also allow pressure to vary in our free energy, more complex behavior can be observed. At first, increasing the pressure in a magnet will simply shift the critical temperature, but not change the critical exponents. In that case the scaling of the pressure is irrelevant, and this can be expressed by setting the power r in λ^r equal to zero. But we could also get things like tri-critical points, and now the story is different.

The other question one can ask is if the free energy is the only possible starting point. The answer is no, any function of two variables can be used as a basis for scaling. One common choice is to start with the pair correlation function, and write:

$$\Gamma(\lambda^x r, \lambda^y \theta) = \lambda \Gamma(r, \theta) \tag{5.139}$$

and derive all critical exponents from the values of x and y. This is not hard to do, since we know that the pair correlation function has the form

$$\Gamma(T, r) = f(\frac{r}{\xi(T)})\xi^u(T) \tag{5.140}$$

with $u = 2 - d - \eta$, and therefore

$$\Gamma(\lambda^x r, \lambda^y \theta) = f(\lambda^{x+y\nu} \frac{r}{\xi(T)})\lambda^{-yu\nu}\xi^u(T) \tag{5.141}$$

which yields:

$$x + y\nu = 0 \tag{5.142}$$

and

$$-yu\nu = 1 \tag{5.143}$$

with solutions

$$y = -\frac{1}{u\nu} = \frac{1}{d\nu - (2-\eta)\nu} = \frac{1}{2\beta} = \frac{p}{2(1-q)} \tag{5.144}$$

Show that $2\beta = d\nu - (2 - \eta)\nu$.

and

$$x = -y\nu = \frac{2-\alpha}{2d\beta} = \frac{1}{2d(1-q)} \tag{5.145}$$

which shows that the two formulations are equivalent.

TIME DEPENDENT PHENOMENA.

In Ginzburg-Landau theory we describe the thermodynamically stable state when we have applied a field at the origin. In a real process we can imagine that at time $\tau = 0$ we apply a magnetization at the origin in a non-magnetic state. The effects of this seed at the origin will propagate outwards, and regions away from the origin will become magnetized. The magnetized region will expand and finally in the limit $\tau \to \infty$ approach the Landau-Ginzburg solution. Since this process is a non-equilibrium process, it is hard to describe in terms of a free energy, but one can easily describe the pair correlation function as a function of time τ by $\Gamma(r, \tau, \theta)$.

DIFFUSION EQUATION.

As we will see later, the change in magnetization over time is described by a diffusion equation:

$$\left(\frac{\partial m}{\partial \tau} \right)_{\theta, \vec{r}} = D\vec{\nabla}^2 m \tag{5.146}$$

where D is the <u>diffusion constant</u>. In our example where we start with a delta function at the origin, $m(r, \tau = 0) = M_0\delta(\vec{r})$ the solution is simple:

$$m(\vec{r}, \tau) = \frac{M_0}{(4\pi D\tau)^{\frac{3}{2}}} e^{-\frac{r^2}{4D\tau}} \tag{5.147}$$

where we see that the size of the magnetized area increases like $\sqrt{\tau}$ as expected. This function $m(\vec{r}, \tau)$ is proportional to $\Gamma(r, \tau, \theta)$.

TIME SCALING.

We now take into account the scaling of the time variable in a straightforward manner:

$$\Gamma(\lambda^x r, \lambda^z \tau, \lambda^y \theta) = \lambda \Gamma(r, \tau, \theta) \tag{5.148}$$

which introduces a new parameter z and hence one new independent critical exponent.

SCALING OF THE DIFFUSION CONSTANT.

The pair correlation function also obeys the diffusion equation, given by:

$$\left(\frac{\partial \Gamma}{\partial \tau}\right)_{\theta, \vec{r}} = D\vec{\nabla}^2 \Gamma \tag{5.149}$$

where the diffusion constant depends on the temperature, and near the critical point is described by an exponent κ:

$$D(\theta) \propto \theta^{-\kappa} \tag{5.150}$$

RELATION BETWEEN Z AND κ.

The derivatives in the diffusion equation also scale with λ and we have

$$\lambda^z \left(\frac{\partial \Gamma}{\partial \tau}\right) (\lambda^x r, \lambda^z \tau, \lambda^y \theta) = \lambda \left(\frac{\partial \Gamma}{\partial \tau}\right) (r, \tau, \theta) \tag{5.151}$$

and

$$\lambda^{2x} \vec{\nabla}^2 \Gamma(\lambda^x r, \lambda^z \tau, \lambda^y \theta) = \lambda \vec{\nabla}^2 \Gamma(r, \tau, \theta) \tag{5.152}$$

which leads to

$$D(\lambda^y \theta) = D(\theta)\lambda^{2x-z} \tag{5.153}$$

which gives

$$\kappa = \frac{z - 2x}{y} = \frac{z + 2y\nu}{y} \tag{5.154}$$

This shows that we can obtain the value of z from a measurement of the diffusion constant and a knowledge of two other critical exponents.

CONSEQUENCES.

If the time scaling in the pair correlation function is not important, and z=0, we find that $\kappa = 2\nu$ and in Ginzburg-Landau theory this gives $\kappa = 1$. Therefore, we expect the diffusion constant to become infinitely large at the critical point. Any small perturbation propagates with very large speed near the critical point. This is, of course, not realistic, and implies that we need to use a relativistic form of the equations. Also, the diffusion equation has a built-in assumption that the diffusion is slow. So details near the critical point are again messy, but the fact that the diffusion constant increases when we approach the critical point can easily be measured.

5.9   Extra equations.

1. *What is the physics determining the nature of the critical exponents?*

2. *What is universality?*

3. *What is the meaning of universality?*

4. *Superconductivity example. Discuss the relation between phase and vector potential.*

5. *What is mean field theory and why is it important?*

6. *Can we find critical exponents in finite systems?*

7. *How do we measure critical exponents?*

8. *What are scaled variables?*

9. *What is the meaning of the fluctuation term in the energy?*

10. *What does scaling of the free energy mean?*

11. *Why do we only scale the fluctuation part?*

12. *Why are there only two independent critical exponents?*

13. *What is the physical meaning of inequalities versus equalities?*

14. *What is the pair correlation function?*

15. *What does scaling of the pair correlation function mean?*

16. *What is hyper-scaling?*

17. *What is a marginal dimension?*

18. *Could we start expansions starting at infinite dimensions?*

19. *What are consequences of mean field theory being correct in 4d?*

20. *Explain time scaling.*

21. *Can the diffusion constant be infinite?*

5.10   Problems for chapter 5

PROBLEM 1.

Derive equation 5.110.

PROBLEM 2.

Show that equation 5.116 for small q is proportional to $q^{\eta-2}$.

PROBLEM 3.

Derive equation 5.153

PROBLEM 4.

A sequence of critical exponents Δ_l , Δ_l' is defined by

$$\left(\frac{\partial^l G}{\partial H^l}\right)_T \propto \left(\frac{T}{T_c} - 1\right)^{-\Delta_l} \left(\frac{\partial^{l-1} G}{\partial H^{l-1}}\right)_T \qquad (5.155)$$

for $l > 0$ and $T > T_c$. The primed exponents are for $T < T_c$, where the pre-factor is $\left(1 - \frac{T}{T_c}\right)^{-\Delta_l'}$. These exponents are called <u>gap exponents</u>. Show that $\Delta_1' = 2 - \alpha' - \beta$ and $\Delta_2' = \beta + \gamma'$. Show that in mean field theory $\Delta_l' = \frac{3}{2}$ for all values of l.

Chapter 6

Transport in Thermodynamics.

6.1 Introduction.

WHAT EXPERIMENTALISTS DO.

Experimental sciences all have one thing in common. You are trying to discover something about a system. There are two ways of doing that. You can sit down and observe the system. This is always the best first step, and one cannot underestimate the importance of this step. But there comes a point in time where observing alone does not give much new information on a time scale of interest. For example, consider a system that shows a very peculiar behavior one hour every three hundred years. This is longer that our life time, and we will be impatient. It is possible for generations of scientists to study this system and write down what they observe. After a thousand years or so we will have good information about that system. The "we" in this context is mankind, not an individual. Our culture, however, does not have that patience, and we will do something about it.

The second step in any experimental discovery is the following. You poke the system and see how it responds. Here we can make several choices. We can poke it gently or violently. What is the difference? If we poke it gently, the system will return to its original state or to a nearby state which we still identify as being part of the original system. If we poke it violently, the system afterwards is completely different from the system before.

Give examples of these two types of investigations.

One of the problems with distinguishing gentle and violent is that we do not know a priori where the border between these two is. Of course, we will have some idea from our careful observations in step one. But even that might not be sufficient. In that case we start with the smallest poke we can do, and observe the reactions. We can only hope that we did it gentle enough.

How do these general remarks translate into the realm of physics? Especially in the context of thermodynamics. That is not too difficult. For example, we have a system and increase its temperature. We wait until the system is again in equilibrium.

How long do we have to wait?

After the waiting time is over we measure whatever we want to measure.

Can we measure without perturbing the system?

From experiments like the one sketched above we find equations of state. For example, the previous experiment could have given us $V(T, p)$ at standard pressure. We can then increase the pressure, too, and map out the whole curve. We will probably discover phase transitions in the material. At that point we need to make a judgement. For example, we see the change from ice to vapor. Is the vapor the same system as the ice or not? The answer depends on the context of our problem! If you are in the situation that ice and vapor are the same system, what if you further increase the temperature and the molecules in the vapor break apart?

In the last case, are we still studying the same system?

Gradients.

In the previous subsection we assumed that the change in control variable (the poke) is uniform over the whole sample. Often that is not true, and we all know that keeping a temperature uniform is hard to do. Again, it is a matter of tolerance. If the deviations from uniformity are small enough **according to a specific standard** we can ignore them. But we can also turn this around. Suppose we make the control variable non-uniform on purpose. For example, we take a block of ice and heat one end with a torch. What happens? Is it interesting?

How large is large?

The question that always needs to be answered is how large is the applied difference of control variable. For example, when we apply a voltage across a material we observe a current. If the voltage is too large, we see a spark. In between, there can be many interesting types of behavior, too. In non-linear dynamics you studied the transitions from uniform convection to convection rolls. There was period doubling en route to chaos. This is all very complicated, and not easy to describe. The only part where we have some hope of success is when the currents are uniform. But even there we need to be careful.

LINEAR RESPONSE ONLY.

We are all familiar with Ohm's law. The current I in response to a voltage difference $\mathcal{V}$ is given by $I = \frac{\mathcal{V}}{R}$. The resistance R for a given piece of material can be measured once and for all, and does not vary for that piece of material if we change the applied voltage. Hence the resistance R is a material's property and only depends on the state of the material. For example, it will depend on the temperature of the material! It also depends on the geometry of the material, however. Make a wire twice as long, and the resistance doubles. This dependence is easy to scale out, though. In stead of the current I we use the current density j, the amount of current passing through a unit area. In stead of the applied voltage we use the electric field E. When the field is constant we have $\mathcal{V} = EL$ where L is the length of the material. If the cross sectional area is A, we arrive at $j = \frac{I}{A} = \frac{EL}{RA}$. The quantity $\frac{RA}{L}$ is called the resistivity of the material, and is a property independent of the geometry. It is more useful to replace it by its inverse, the conductivity σ. Also, we have to realize that both current and field are vector quantities and hence we write in general:

$$\vec{j} = \sigma \cdot \vec{E} \tag{6.1}$$

where in the general case σ is a tensor, a three by three matrix in this case. In cubic materials, however, the conductivity is simply a number times the unit matrix. But in layered materials we know that the conductivity parallel to the layers is different from the conductivity perpendicular to the layers!

HIGHER ORDER TERMS.

In general, the conductivity σ depends on the external field, and this dependence can be very complicated. We restrict ourselves to the low field limit. In that case we can write:

$$\vec{j} = \sigma_1 \cdot \vec{E} + \sigma_2 \cdot \vec{E}\vec{E} + \cdots \tag{6.2}$$

and the coefficients in the Taylor expansion are independent of the field. The second order conductivity is also a materials property, but is not used very often. Hence we will assume that this term is not important, and only use linear response.

Discuss types of experiments that measure higher order response terms.

Typical transport situations.

There are a number of cases where transport is important. For example, we can study the flow of gas through pipes. From a technical point of view, this is a very important application. The important parameters are pressure and temperature. In this scenario one typically follows the fluid while it is flowing through the system, but that is not necessary. I will not discuss this application here, since I know the basics only. That is my shortcoming, however, and does not reflect at all on the importance of the subject!

The application I will use as an example is conductivity in a solid. If we apply an electric field we will induce a current. In solids the pressure is typically constant at standard pressure, and we will ignore pressure as a variable. This allows us to discuss the process in terms of densities as shown later. But temperature is an important control parameter, as is magnetic field. We will not include magnetic field effects extensively, however. This is a detail only, and is easy to incorporate, as long as one is aware of extra minus signs. These minus signs are due to the fact that reversing a current is equivalent to time reversal, but that only works when one also inverts the magnetic fields.

Steady state.

Another important point is that we will only discuss transport in the steady state. We assume that all transients due to changes in the control parameters have died out. Hence there are no time dependencies in the applied fields, and we can write $\vec{E}(\vec{r})$ and $T(\vec{r})$. Since there are currents, there is time dependence in corresponding extensive parameters. Something is moving! For example, in our case we follow the electrons in a solid. The electrons are the vehicle for the electric current. In a steady state, the number of electrons in a certain volume is constant, and equal numbers of electrons are moving in and out. We also assume that there are enough collisions that these electrons are in thermal equilibrium with the ions in the solid, and have the same temperature. Therefore, the length scale implead by the applied external field should be long compared to the mean free path of the electrons. Hence we do not discuss so-called ballistic transport, where electrons shoot through a medium without interactions. These kind of processes need a different framework of description.

In our application heat is a transport of energy by both the electrons and by the ions in the solid, via lattice vibrations. We will not discuss the latter part, but real experiments will always have to take that contribution into account!

6.2 Some thermo-electric phenomena.

Electric conductivity is a very familiar example of a transport phenomenon. It is so familiar, that we easily make mistakes in using conductivity! The naive approach is to apply a voltage difference to a sample and to measure the current. Why is this naive? Because we need to connect the sample to the voltage source and the current meter! These wires have their own resistance, but even more important, the contact between the wires and the sample have resistance.

An improvement is to reverse the procedure. A known current is driven through a sample. In a steady state there is no accumulation of charge, and we know that all the current leaving the current source will go through the sample. Well, at least as long as there are no leaks! We than take two different wires and connect these to the sample in between the current leads. We measure the voltage difference between these wires, and from that derive the resistance. We do not worry about the resistivity of the contacts, since the driving current does not pass though them, and since the measuring current can be made extremely small. A very ingenious method indeed!

Can there be a problem? Yes! Several, actually. Because there is resistance, there will be a production of thermal energy. In such a case we can either keep the temperature constant or do the measurement in an adiabatic fashion. Would that make a difference? It probably will! Later we will show that it indeed does make a difference, and that the adiabatic conductivity is different from the constant temperature conductivity.

What else could go wrong? The temperature in the steady state of the experiment might not be uniform! In that case the contacts used for measuring the voltage difference could be at different temperatures, which is known to have consequences!

THERMOCOUPLES.

Consider the setup in figure 6.1. Two different materials (A and B) are used. Material B is cut in the middle, and the ends are connected to input leads. At these input leads we can either apply a voltage or drive a current. The connections between material A and B are at two different temperatures T_1 and T_2. During the experiment there will also be heat going through both materials. Since thermal energy will also be produced everywhere there will be a heat flow out of the materials into the environment, represented by the arrows in figure 6.1. We will now use this device in several setups.

SEEBECK EFFECT.
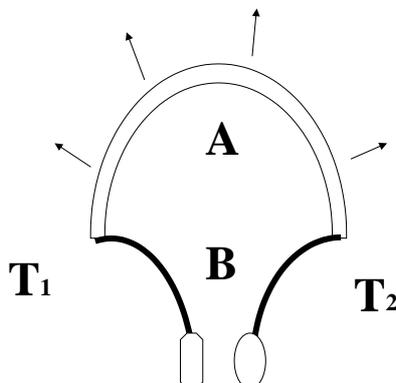
Figure 6.1: **Essential geometry of a thermocouple.**

We measure the voltage difference $\mathcal{V}$ between the input leads when there is a temperature difference between the endpoints. In this case there is no electric current through the thermocouple. The voltage difference depends on the materials A and B only, and for small temperature differences we have

$$\mathcal{V} = -\alpha_{AB}(T_2 - T_1) \tag{6.3}$$

where we define the signs in the following manner. If $T_1 > T_2$ and if the thermocouple were connected to a resistor, the coefficient α_{AB} is positive if the resulting electric current goes from point 1 to point 2 through material A and returns through material B and the resistor. If we label the input leads by 1 and 2 according to which end they are connected to, we have $\mathcal{V} = V_2 - V_1$. The extra minus sign in the definition of α is due to the distinction between internal and external currents, which follow an opposite path. This effect, the Seebeck effect, was discovered in 1821! Note that this is before the discovery of Ohm's law!

How can we use the Seebeck effect in a practical manner?

PELTIER EFFECT.

We can also do the opposite. We drive a current I through the thermocouple. The current is positive if we drive it similar to the previous subsection. The current is driven into lead 1 and extracted at lead 2, if positive. In this case a positive amount of heat Q is generated at connection 1 between materials A and B and the same amount of heat is absorbed at the other end, connection 2. In addition to this heat flow between 2 and 1 there is, of course, also extra

heat generated all along the path, because we have both electric and thermal currents. But the <u>Peltier effect</u> only relates the heat flow between 1 and 2 and we have

$$Q = \Pi_{AB} I \tag{6.4}$$

This effect was discovered only ten years or so after the Seebeck effect. It has one very important application. We can use the Peltier effect to cool a sample connected to lead 2!

Kelvin found an empirical relation between the Seebeck effect and the Peltier effect in 1854:

$$\Pi_{AB} = T\alpha_{AB} \tag{6.5}$$

THOMSON HEAT.

Suppose we have both a heat flow and an electric current through the thermocouple. In that case heat is generated at every point along the thermocouple. This is represented by the arrows in figure 6.1. Suppose the distance along material A (or B) is measured by a parameter x. The heat generated at position x in an interval Δx is given by ΔQ, and Thomson found that

$$\Delta Q = \tau I \frac{dT}{dx} \Delta x \tag{6.6}$$

He also derived (empirically!) that

$$\tau_A - \tau_B = T\frac{d\alpha_{AB}}{dT} \tag{6.7}$$

Note that the coefficients defined so far always depend on the difference between two materials. Nowadays we use a reference material at all temperatures, and define the absolute thermoelectric coefficients with respect to this standard. For the absolute values we also have

$$\tau = T\frac{d\alpha}{dT} \tag{6.8}$$

What is the relation between Thomson and Kelvin?

MAGNETIC EFFECTS.

When we apply a magnetic field perpendicular to the thermocouple, the Lorentz force gives a sideways displacement of the charge carriers. These are transverse effects. The following four combinations are useful:

- **Hall**: Drive an electric current through the material and measure the transverse electric field.

- **Nernst**: Drive a heat flow through the material and measure the transverse electric field.

- **Ettingshausen**: Drive an electric current through the material and measure the transverse temperature gradient.

- **Righi-Leduc**: Drive a heat flow through the material and measure the transverse temperature gradient.

For detailed discussions see books on solid state physics.

6.3   Non-equilibrium Thermodynamics.

IS IT POSSIBLE?

The words non-equilibrium thermodynamics do not seem to make sense at first glance. By definition, thermodynamics describes a material in equilibrium, and it is only then that we are able to have equations of state. If we are not in equilibrium, some state functions do not have their correct values (the entropy is not maximal, or some free energy is not minimal), and there is no correct mathematical description.

In order to discuss the situation presented above, we need to consider the microscopic details of the material, and follow a system as a function of time by solving the equations of motion. This leads to concepts like chaotic dynamics, and some very interesting physics. Boltzmann was probably one of the first to give a beginning of an answer to this problem.

WHEN DEVIATIONS ARE SMALL.

What happens when a system is almost in equilibrium? When the deviations from equilibrium are small? Perturbation theory should apply, and a complete knowledge of the equilibrium state should be sufficient to understand what is happening. This is the situation in which we can still use the formulas from equilibrium thermodynamics, and discuss what happens when we are not quite in equilibrium.

LOCAL STABILITY.

Suppose we divide our materials in small cells, with volume ΔV each. In each cell, with position $\vec{r}_i$ we have a an amount of material ΔN_i and a temperature T_i. We assume that the material in each cell is **internally** in thermodynamic

equilibrium. Therefore, the usual equations of state will give us the values of the other state variables p_i, μ_i, and S_i, as well as the energy U_i. We assume that we deal with the standard pVT system, if not we need to add one variable for each additional pair to the set of variables that we need to know. This scenario is called local stability.

LIMITS.

In order for local stability to exist, the volume ΔV needs to be large. What is large? In general, this volume needs to contain many molecules. On the other hand, we would like to evaluate quantities like $N = \sum_i \Delta N_i$ via integrals. If we define the density in cell i by $n_i = \frac{\Delta N_i}{\Delta V}$ we would like to replace

$$\sum_i n_i \Delta V \Rightarrow \int n(\vec{r}) d^3 r \qquad (6.9)$$

and in order to do so we need to take the limit $\Delta V \to 0$, which obviously causes problems. The answer is again found by assuming that the variations in the density and temperature are small. This implies that, if we follow the Riemann sum $\sum_i n_i \Delta V$ as a function of decreasing value of ΔV, this sum reaches a stable (converged) value while the volume ΔV is still large on a microscopic scale. At that point we stop and do not enter the region where ΔV becomes so small that we see the effects of the microscopic structure.

TESTS FOR VALIDITY.

The ideas developed in the previous paragraph give us a definition when we can still use the equations of thermodynamics, but also allow for fluctuations. It also gives a recipe for a numerical test of this condition. We divide space in cells and calculate all quantities with the given cell size. Next, we choose smaller cells, and recalculate all our quantities. This gives us a plot of the value of the quantity versus cell size. By extrapolating these values to those obtained with $\Delta V = 0$ we find the error in our calculations for each cell size. On the other hand, we also have an error due to the fact that our cells only contain a finite number of particles. This is an error not included in the calculations above, and has to be added. This error is of the form $\frac{1}{\sqrt{\Delta N_i}}$, which can be approximated by $\sqrt{\frac{N}{V}} \frac{1}{\Delta V}$. Adding these terms together we get a minimum error at some optimal value of the cell size, and if this minimal error is acceptable, our model is useful. If not, the spatial variations in the density are too fast. From now on we will assume that our procedure gives acceptable results according to this test.

CHOICE OF FIELDS.

In a standard pVT system we need to specify three state variables to completely identify the state. At each position $\vec{r}$ we fix the volume d^3r and hence we need two other state variables to completely specify what is happening. Conceptually the easiest are $n(\vec{r})$ and $T(\vec{r})$, because we can imagine that these can be measured very well. But we could also choose quantities like the energy density $u(\vec{r})$, which can have advantages in the theoretical formulations.

Different coordinate frames.

Another choice which is often made is to use cells that contain a fixed amount of material ΔN. In this case the cells have variable volume $d^3v = n(\vec{r})d^3r$, but all formulas can be derived by simply adding this weight function. All densities in this case are per mole, and not per unit volume as in the previous case.

Sometimes we want to study liquids that support macroscopic currents. At each point we find a velocity field $\vec{v}(\vec{r})$ which tells us in which direction the liquid is flowing at that point. It can be very useful to use a coordinate frame that is moving with the liquid and to follow the amount of material in the original cell.

Work between cells.

In our formulation the size of the cells is fixed, and mechanical work of the pdV variety is therefore not possible. The only two ways the cells can exchange energy with each other is to do chemical work μdN, which is an exchange of material between the cells, or use heat transfer TdS. Of course, if we would have chosen cells with a fixed amount of material, the situation would be different and we could use mechanical work as well as heat.

6.4   Transport equations.

Slow processes only.

In the previous section we have developed a model in which we have local equilibrium, because densities are varying slowly in space. But because there is a change in density and temperature between cells, there will be a flow of material and heat in order to reach equilibrium. We will assume that this flow is **very slow**. In other words, the local densities are changing, but at a rate which is much slower than the rate in which these cells get back to equilibrium after a small amount of material or heat has been exchanged. This is a natural consequence of the assumption that the system is **always** in local equilibrium. If transport is too fast, we cannot maintain local equilibrium.

Continuity equation.

If we consider an arbitrary small volume ΔV and follow the change of an extensive quantity X in that volume, the change $\frac{d\Delta X}{dt}$ in that quantity is the sum of the creation and/or destruction of X and the flow of X through the surface ΔS of the volume element. The flow is given by a current density $\vec{J}_X$ by following the amount of X going through an area ΔA with surface normal $\hat{n}$ in a time Δt. The corresponding amount of X flowing through this area is

$$\Delta X = \vec{J}_X \cdot \hat{n} \Delta A \Delta t \tag{6.10}$$

Therefore, the rate of change in X is

$$\frac{d}{dt} \int_{\Delta V} x d^3 V = \int_{\Delta V} P_x(\vec{r}, t) d^3 V - \oint_{\Delta S} \vec{J}_X \cdot \hat{n} d^2 S \tag{6.11}$$

where the first term on the right, P_x, is the local creation (which could be negative) per unit volume and the second term the flow through the surface. The quantity x is the density of X, or the amount of X per unit volume. The surface normal in this definition points outwards from the volume element. Using Gauss' theorem this gives

$$\frac{d}{dt} \int_{\Delta V} x d^3 V = \int_{\Delta V} P_x d^3 V - \int_{\Delta V} \vec{\nabla} \cdot \vec{J}_X d^3 V \tag{6.12}$$

and since the volume is arbitrary we have at each point in space:

$$\frac{\partial x}{\partial t} = P_x - \vec{\nabla} \cdot \vec{J}_X \tag{6.13}$$

We have replaced the total derivative by a partial derivative, since we look at the change of $x(\vec{r}, t)$ at each point. The production is sometimes written as a time derivative, too, and in order to distinguish one uses a notation like

$$P_x = \frac{Dx}{Dt} \tag{6.14}$$

This notation (or variations of it), is widely used in physics, and it reflects the change in quantity X due to both creation and transport. In a coordinate frame moving with the liquid this is the only term that survives, which is a main reason for choosing such a frame. The continuity equation is in this notation:

$$\frac{Dx}{Dt}(\vec{r}, t) = P_x(\vec{r}, t) = \frac{\partial x}{\partial t}(\vec{r}, t) + \vec{\nabla} \cdot \vec{J}_X \tag{6.15}$$

Is $\frac{Dx}{Dt}$ a real derivative?

EXTENSIVE STATE PROPERTIES ARE CONSERVED.

Consider two adjacent cells. If material flows from one cell to the other, the total amount of material does not change. In other words, if a cell looses material, this material is not created or destroyed, but transported to neighboring cells. For example, the energy of one cell changes because energy is flowing in to or out of the cell. We assume that we do not have any chemical reactions, and there is no creation of energy or material. Hence we assume that

$$P_u(\vec{r}, t) = 0 \tag{6.16}$$

$$P_n(\vec{r}, t) = 0 \tag{6.17}$$

Since energy and material are conserved, we now have

$$\vec{\nabla} \cdot \vec{J}_U = -\frac{\partial u}{\partial t} \tag{6.18}$$

and

$$\vec{\nabla} \cdot \vec{J}_N = -\frac{\partial n}{\partial t} \tag{6.19}$$

where u is the energy density and n is the matter density. Note that the inclusion of chemical reactions is conceptually not difficult, just tedious, because now we need to distinguish between several types of material and have to include partial time derivatives.

ENTROPY PRODUCTION AND FLUXES.

Consider a cell which is divided in to two equal parts by an area ΔA with surface normal $\hat{n}$ pointing from the left to the right. The width of each half is $\frac{1}{2}\Delta L$. The left side of this cell changes its energy by an amount ΔU_l and its amount of material by ΔN_l. Because we always have local equilibrium, we know that $\Delta U_l = T_l \Delta S_l + \mu_l \Delta N_l$ in this part of the cell. If we assume no contact outside the cell, the material and energy need to come from the right part of the cell, and therefore we have

$$\Delta U_l = -\Delta U_r \tag{6.20}$$

$$\Delta N_l = -\Delta N_r \tag{6.21}$$

But local equilibrium gives us the conditions that $\Delta U_r = T_r \Delta S_r + \mu_r \Delta N_r$ for that half of the cell. Therefore we find that

$$\Delta S_l + \Delta S_r = \frac{1}{T_l} \Delta U_l - \frac{\mu_l}{T_l} \Delta N_l + \frac{1}{T_r} \Delta U_r - \frac{\mu_r}{T_r} \Delta N_r \tag{6.22}$$

or by using the conservation laws we find that the entropy production is

$$\Delta S_l + \Delta S_r = (\frac{1}{T_r} - \frac{1}{T_l})\Delta U_r + (\frac{\mu_l}{T_l} - \frac{\mu_r}{T_r})\Delta N_r \qquad (6.23)$$

The amount of energy flowing through the area ΔA is ΔU_r and the amount of material ΔN_r, all in a time Δt. If the local energy current density at the origin is $\vec{J}_U$ and the local material current density $\vec{J}_N$, then we have

$$\Delta U_r = \vec{J}_U \cdot \hat{n}\Delta A\Delta t \qquad (6.24)$$

$$\Delta N_r = \vec{J}_N \cdot \hat{n}\Delta A\Delta t \qquad (6.25)$$

The entropy produced in this process is given by

$$\Delta S = \Delta S_l + \Delta S_r = \left((\frac{1}{T_r} - \frac{1}{T_l})\vec{J}_U \cdot \hat{n} + (\frac{\mu_l}{T_l} - \frac{\mu_r}{T_r})\vec{J}_N \cdot \hat{n} \right)\Delta A\Delta t \qquad (6.26)$$

This can be related to the gradients in the following manner:

$$\frac{1}{T_r} - \frac{1}{T_l} = \vec{\nabla}\left(\frac{1}{T}\right) \cdot \hat{n}\frac{1}{2}\Delta L \qquad (6.27)$$

and similar for the second term. This gives:

$$\Delta S = \frac{1}{2}\left(\vec{\nabla}\left(\frac{1}{T}\right) \cdot \hat{n}\vec{J}_U \cdot \hat{n} - \vec{\nabla}\left(\frac{\mu}{T}\right) \cdot \hat{n}\vec{J}_N \cdot \hat{n}\right)\Delta A\Delta L\Delta t \qquad (6.28)$$

and therefore the rate of change of the production of the entropy density s (entropy per unit volume) for this process is given by:

$$P_s = \frac{1}{2}\left(\vec{\nabla}\left(\frac{1}{T}\right) \cdot \hat{n}\vec{J}_U \cdot \hat{n} - \vec{\nabla}\left(\frac{\mu}{T}\right) \cdot \hat{n}\vec{J}_N \cdot \hat{n}\right) \qquad (6.29)$$

In this equation we have chosen an arbitrary direction of the dividing partition. Of course, we need to take into account the complete flow. Consider a small cubic cell with faces orthogonal to the x, y, and z direction. The local entropy density production for the flow through each of the faces of this cube is given by the expression above, with either $\hat{n} = \pm\hat{x}$, $\hat{n} = \pm\hat{y}$, or $\hat{n} = \pm\hat{z}$. We can use the expression for one side of the partition only, since we use the entropy density, or entropy per unit volume! If we add the effects the flow through all sides of the cube together we get the total entropy density production in this cubic cell. It is easy to see that

$$\sum_{\hat{n}}(\vec{A} \cdot \hat{n})(\vec{B} \cdot \hat{n}) = 2A_x B_x + 2A_y B_y + 2A_z B_z = 2\vec{A} \cdot \vec{B} \qquad (6.30)$$

and hence the expression for the total energy density production is

$$P_s = \left(\vec{\nabla} \left(\frac{1}{T} \right) \cdot \vec{J}_U - \vec{\nabla} \left(\frac{\mu}{T} \right) \cdot \vec{J}_N \right) \tag{6.31}$$

Note that using a cubic cell is not essential, it just makes the mathematics much easier. Also note that we get a factor two, because at each point we need to consider the flow into that point from one side and the flow out of that point towards the other side!

What does P_s exactly mean?

ENTROPY FLOW.

Next we define the flow of entropy $\vec{J}_S$ by relating it to the flow of energy and the flow of particles.

$$\vec{J}_S = \left(\frac{1}{T} \right) \vec{J}_U - \left(\frac{\mu}{T} \right) \vec{J}_N \tag{6.32}$$

As a consequence we find that

$$\vec{\nabla} \cdot \vec{J}_S = \left(\frac{1}{T} \right) \vec{\nabla} \cdot \vec{J}_U - \left(\frac{\mu}{T} \right) \vec{\nabla} \cdot \vec{J}_N + \vec{\nabla} \left(\frac{1}{T} \right) \cdot \vec{J}_U - \vec{\nabla} \left(\frac{\mu}{T} \right) \cdot \vec{J}_N \tag{6.33}$$

and using the continuity equations for the energy and material current we obtain:

$$\vec{\nabla} \cdot \vec{J}_S = - \left(\frac{1}{T} \right) \frac{\partial u}{\partial t} + \left(\frac{\mu}{T} \right) \frac{\partial n}{\partial t} + \vec{\nabla} \left(\frac{1}{T} \right) \cdot \vec{J}_U - \vec{\nabla} \left(\frac{\mu}{T} \right) \cdot \vec{J}_N \tag{6.34}$$

Since we always have local equilibrium, we can use the first law of thermodynamics:

$$dU = TdS + \mu dN \tag{6.35}$$

and show the sum of the first two terms is equal to $-\frac{\partial s}{\partial t}$ and hence we find that for the local production of entropy we get

$$P_s = \left(\vec{\nabla} \left(\frac{1}{T} \right) \cdot \vec{J}_U - \vec{\nabla} \left(\frac{\mu}{T} \right) \cdot \vec{J}_N \right) \tag{6.36}$$

as we derived before. This justifies that we defined the entropy current correctly.

Why is $-\frac{\partial s}{\partial t} = - \left(\frac{1}{T} \right) \frac{\partial u}{\partial t} + \left(\frac{\mu}{T} \right) \frac{\partial n}{\partial t}$?

In our example we assume that locally we have a pVT system, and because we define subregions by constant volume elements, only energy and mass can flow. In a more general case, we could also include other quantities, like the flow of magnetization. In this case we have for the first law in each local cell (with $dV = 0$) an equation of the form:

$$TdS = \sum_i x_i dX_i \qquad (6.37)$$

which after dividing by T takes the form:

$$dS = \sum_i \phi_i dX_i \qquad (6.38)$$

Therefore, we have in the general case:

$$\vec{J}_S = \sum_i \phi_i \vec{J}_i \qquad (6.39)$$

and

$$P_s = \sum_i \vec{\nabla}\phi_i \cdot \vec{J}_i \qquad (6.40)$$

In general, each current will depend on the values of all intensive parameters and their gradients. We have to keep in mind, however, that we assume that we are close to equilibrium. If all intensive parameters are constant, we are in equilibrium, and no net macroscopic flows are present. When we are close to equilibrium, the gradients in the intensive parameters will be small, and as a consequence we can expand the formulas for the currents in terms of the gradients of the intensive parameters. An important case in practice is the situation where the gradients are so small that we need only linear terms. We will restrict ourselves to that case and only study <u>linear processes</u>. The basic equations are now

$$\vec{J}_i = \sum_k \mathcal{L}_{ik} \cdot \vec{\nabla}\phi_k \qquad (6.41)$$

where the matrix coefficients $\mathcal{L}_{ik}$ are functions of the intensive parameters (or of the combinations ϕ_i) only. The currents we consider here are only currents in energy, matter, etc. and not in the entropy. Of course, we can always eliminate one of these currents in favor of the entropy current. This has the advantage that we now have heat transport included as a separate entity.

Are the variables $\mathcal{L}_{ik}$ state functions?

ONSAGER RELATIONS.

The coefficients $\mathcal{L}_{ik}$ in the last formula obey some symmetry relations. This is directly related to the fact that fluctuations are not completely arbitrary, but are related to the entropy as described in chapter two. The other ingredient is time reversal symmetry. The general form of the relation in the presence of a magnetic field is:

$$\mathcal{L}_{ik}(T, \mu, \vec{H}) = \mathcal{L}_{ki}^{T}(T, \mu, -\vec{H}) \qquad (6.42)$$

where the transpose indicates a transpose of the three by three matrix in coordinate space. Because magnetic fields give velocity dependent forces, we need to change the sign of the field when we reverse the direction of time. This is the cause for the minus sign in the last equation. There are also **additional minus signs** in front of the equations for properties that mix magnetic and non-magnetic transport.

6.5   Macroscopic versus microscopic.

THERMAL AVERAGES.

In each cell we can define the local values of the extensive variables X_i and corresponding intensive variables ϕ_i. As mentioned before, we assume local equilibrium, and these variables are connected by equations of state. If there are no external fields, all these values are independent of position and time. If there is an external field, however, the values in different cells will not be the same anymore. For example, we can imagine that there is a temperature field $T(\vec{r}, t)$ present, and we want to study its consequences. Because we assume local equilibrium, the spatial and temporal variation of this field has to be small. This implies that we can only study the long wavelength and low frequency response of a system.

The results will break down when either the wavelength is too small or the frequency is too high, and microscopic effects start to play a role. In the next sub-sections we relate the microscopic and macroscopic views, which also provides a proof for Onsager's relations. We do this in a general manner, independent of the microscopic nature of the material. We simply consider the fluctuations in each cell. Some of the parameters describing these fluctuations, however, can only be calculated in a microscopic theory. This is similar to the situation in the Landau-Ginzburg theory as discussed in Chapter 4.

FLUCTUATIONS.

Assume that the equilibrium system is determined by local values $X_i^0(\vec{r}, t)$ of the extensive parameters in each cell. Then in our non-equilibrium state we

have in a given cell at point $\vec{r}$ the values $X_i(\vec{r}, t) = X_i^0(\vec{r}, t) + \delta X_i(\vec{r}, t)$. The fluctuations are small if our cells contain many atoms (which is only possible in the long wavelength limit of external fields). If we now take a thermal average in each cell we find:

$$\langle \delta X_i(\vec{r}, t) \rangle = 0 \tag{6.43}$$

and

$$\langle X_i(\vec{r}, t) \rangle = X_i^0(\vec{r}, t) \tag{6.44}$$

Since a thermal average is equivalent to a time average, we assume that the fluctuations are much more rapid than the variations in the external fields. In that case we are able to do a time average of the quantity $\delta X_i(\vec{r}, t)$ over a time long enough that it represents the thermodynamic limit, but short on the scale of the external perturbations. This is the reason for the low frequency limit.

The fluctuations describe deviations from thermal equilibrium, and hence the quantities $X_i(\vec{r}, t)$ and corresponding fields $\phi_i(\vec{r}, t)$ do not obey the equations of state. Only the average quantities $X_i^0(\vec{r}, t)$ and $\phi_i^0(\vec{r}, t)$ do. The transport equations derived in the previous section use these local thermal equilibrium values, and are defined in that context only.

CORRELATION FUNCTIONS.

The fluctuations mentioned above are correlated, as we described in chapter two. Since the decay of fluctuations follows the laws of physics on the microscopic level, this correlation continues in time and we can discuss correlation coefficients of the form:

$$\langle \delta X_i(\vec{r}, 0) \delta X_j(\vec{r}', t) \rangle \tag{6.45}$$

We can discuss correlations between fluctuations at difference points, since any excess in some extensive parameter has to flow away through neighboring cells. Again, we take averages to avoid all short time thermal fluctuations, and we still assume that the cells are large compared to the detailed structure in the matter. Since the laws of nature are time invariant (here we assume that there are no magnetic fields!) we have:

$$\langle \delta X_i(\vec{r}, 0) \delta X_j(\vec{r}, t) \rangle = \langle \delta X_i(\vec{r}, 0) \delta X_j(\vec{r}, -t) \rangle \tag{6.46}$$

and since we have translational symmetry in time:

$$\langle \delta X_i(\vec{r}, 0) \delta X_j(\vec{r}, t) \rangle = \langle \delta X_i(\vec{r}, t) \delta X_j(\vec{r}, 0) \rangle \tag{6.47}$$

From this equation we subtract $\langle \delta X_i(\vec{r}, 0) \delta X_j(\vec{r}, 0) \rangle$ and in the limit of small t we find

$$\langle \delta X_i(\vec{r}, 0) \frac{\partial \delta X_j}{\partial t}(\vec{r}, 0) \rangle = \langle \frac{\partial \delta X_i}{\partial t}(\vec{r}, 0) \delta X_j(\vec{r}, 0) \rangle \tag{6.48}$$

Next we consider the current density that is related to the quantity δX_i in our cell, and call this current $\overrightarrow{\delta J_i}$. By using the symbol δ we make explicitly clear that this is a microscopic current, related to fluctuations. Because there is no local creation one has:

$$\frac{\partial \delta X_j}{\partial t} = -\vec{\nabla} \cdot \overrightarrow{\delta J_j} \tag{6.49}$$

This leads to

$$\langle \delta X_i (\vec{\nabla} \cdot \overrightarrow{\delta J_j}) \rangle = \langle (\vec{\nabla} \cdot \overrightarrow{\delta J_i}) \delta X_j \rangle \tag{6.50}$$

where we have dropped the space and time arguments, since all quantities are at the same position $\vec{r}$ and same time t. This is important. If we want to relate fluctuations in quantities at different positions and times, we need the probability functions for these correlations, and we have no idea what they look like. On the other hand, probabilities for fluctuations at a given place and time have been discussed in chapter 2, and hence we do know how to calculate them. Therefore, we do have the means to evaluate expressions like the last one.

FLUCTUATIONS IN FIELDS.

The local state of the system is specified by the extensive variables $X_i(\vec{r}, t) = X_i^0(\vec{r}, t) + \delta X_i(\vec{r}, t)$ in each cell positioned at $\vec{r}$. Again, remember that these cells are large enough to contain enough sufficient material to be able to define local thermal equilibrium, but that they are small on the scale of the variations in the externally applied fields. Because we have

$$dS = \sum_i \phi_i dX_i \tag{6.51}$$

we have locally that

$$\phi_i = \left(\frac{\partial S}{\partial X_i} \right) \tag{6.52}$$

where the partial derivatives only vary one of the extensive variables at a time. We assume local equilibrium, and hence

$$\phi_i^0 = \left(\frac{\partial S}{\partial X_i} \right) (X_1^0, X_2^0, \cdots) \tag{6.53}$$

at each point $\vec{r}$ and each time t.

In thermodynamics, intensive quantities like temperature and pressure are only defined in the thermodynamic limit, as average quantities. Fluctuations in extensive quantities are easy to measure, at least in theory. We simply count the amount of material, measure the volume, and measure the energy. Of course, we often only measure changes, but that does not change the picture. Intensive quantities like temperature and pressure are measured using thermal contact

with reservoirs, implying the need of thermal equilibrium. But even though we cannot technically measure these quantities at the level of fluctuations, we can easily define them by:

$$\phi_i(\vec{r}, t) = \left(\frac{\partial S}{\partial X_i} \right) (X_1(\vec{r}, t), X_2(\vec{r}, t), \cdots) \qquad (6.54)$$

For small fluctuations we have

$$\phi_i(\vec{r}, t) = \phi_i^0(\vec{r}, t) + \sum_k \left(\frac{\partial^2 S}{\partial X_i \partial X_k} \right) (X_1^0, X_2^0, \cdots) \delta X_k(\vec{r}, t) \qquad (6.55)$$

or

$$\delta \phi_i(\vec{r}, t) = \phi_i(\vec{r}, t) - \phi_i^0(\vec{r}, t) = \sum_k S_{ik} \delta X_k(\vec{r}, t) \qquad (6.56)$$

where the matrix S is symmetric.

This same matrix also is used in the probability function for small fluctuations in the Gaussian approximation (see Chapter 2), where we have

$$W(\delta X_1, \delta X_2, \cdots) = A e^{\frac{1}{2k_B} \sum_{ij} S_{ij} \delta X_i \delta X_j} \qquad (6.57)$$

We divided the change in entropy by the Boltzmann constant in order to have a dimensionless quantity in the exponent. This also gives

$$\left(\frac{\partial W}{\partial \delta X_k} \right) = k_B^{-1} W \delta \phi_k \qquad (6.58)$$

According to the maximum entropy principle, the probability function W takes its maximal value when all fluctuations are zero. This implies that the exponent in the probability function is always negative for non-zero fluctuations. Since the matrix S_{ij} is real and symmetric, it has a complete set of real eigenvalues. All these eigenvalues are negative, or else there would be fluctuations for which the probability did not decrease. When all eigenvalues are negative, the inverse of the matrix S_{ij} exists. We call this matrix T_{ij} and we therefore find that:

$$\delta X_j = \sum_i T_{ji} \delta \phi_i \qquad (6.59)$$

and because S is symmetric, T is symmetric too.

Finally, we consider the thermal average of the following quantity:

$$\langle \delta X_i \delta \phi_k \rangle = \int \delta X_i \delta \phi_k (\delta X_1, \delta X_2, \cdots) W(\delta X_1, \delta X_2, \cdots) d\delta X_1 d\delta X_2 \cdots \quad (6.60)$$

Because of the relation derived in 6.58 we have

$$\langle \delta X_i \delta \phi_k \rangle = k_B \int \delta X_i \left(\frac{\partial W}{\partial \delta X_k} \right) (\delta X_1, \delta X_2, \cdots) d\delta X_1 d\delta X_2 \cdots \qquad (6.61)$$

and integration by parts then gives

$$\langle \delta X_i \delta \phi_k \rangle = -k_B \delta_{ik} \qquad (6.62)$$

This also gives us a representation for the matrix T, because

$$\langle \delta X_i \delta X_j \rangle = \sum_k T_{jk} \langle \delta X_i \delta \phi_k \rangle = -k_B \sum_k T_{jk} \delta_{ik} = -k_B T_{ji} \qquad (6.63)$$

This also shows the symmetry of the matrix T in an explicit manner. This relation follows, of course, directly from the definition of the probability distribution in 6.57 given above. Similarly we find that

$$\langle \delta \phi_i \delta \phi_j \rangle = \sum_k S_{jk} \langle \delta \phi_i \delta X_k \rangle = -k_B \sum_k S_{jk} \delta_{ik} = -k_B S_{ji} \qquad (6.64)$$

NEED FOR INTERACTIONS.

In the previous discussion there is one important element missing. The forces responsible for currents are the gradients of intensive state variables, $\vec{\nabla} \phi_i$. The probabilities for fluctuations in a cell only depend on the values of the extensive state variables X_i. In order to find the value of the gradient in such a field, we need to consider fluctuations in adjacent cells. They are uncoupled, however, in our current approximation. Therefore,

$$\langle (\delta X_i(\vec{r}) - \delta X_i(\vec{r}'))^2 \rangle = \langle \delta X_i^2(\vec{r}) \rangle + \langle \delta X_i^2(\vec{r}) \rangle \qquad (6.65)$$

and the magnitude of this fluctuation is proportional to the volume of the cell. If we now consider two adjacent cubic cells of dimension L^3 we see that the typical value of the difference in the density is proportional to $L^{\frac{3}{3}}$ and hence a typical value of the gradient is proportional to $\sqrt{L}$. Hence typical values of gradients of densities are proportional to L^{-1} and they become very large for small values of L!

Two things are missing in this approximation. First, extensive quantities are conserved, and if values increase in one cell, the amount has to come from somewhere, and therefore values in neighboring cells tend to decrease. Second, there are interactions between the material in one cell and in another. There is always gravity, and there are forces like the van der Waals interaction. In ionic fluids direct Coulomb interactions are possible. These effects are easily introduced in a microscopic theory, but then the calculations are quite difficult. In thermodynamics we can do the same as we did in chapter four, however, and assume that fluctuations are small and that we can expand in a power series.

The probability of fluctuations in a cell is now described by:

$$W(\delta X_1, \delta X_2, \cdots, \partial_a \delta X_1, \cdots) = A e^{\frac{1}{k_B}\mathcal{S}} \tag{6.66}$$

with

$$\mathcal{S}(\delta X_1, \delta X_2, \cdots, \partial_a \delta X_1, \cdots) = \frac{1}{2}\sum_{ij} S_{ij}\delta X_i \delta X_j + \frac{1}{2}\sum_{iajb} F_{iajb}\partial_a \delta X_i \partial_b \delta X_j$$
$$\tag{6.67}$$

The summations over a and b are summations over Carthesian coordinates. Because the tensor F_{iajb} is related to a second order functional derivative, it is symmetric. Therefore, it has a complete spectrum of eigenvalues, and again all these eigenvalues have to be negative in order to guarantee that the state without fluctuations has the highest probability. Because none of the eigenvalues are zero, the tensor has an inverse.

The definition above is the only one possible in second order, and any microscopic theory has to reduce to this form in lowest order. The values of F_{iajb} can only be calculated in a microscopic theory. This is a fundamental difference with the values of S_{ij} which follow from standard thermodynamics. Note that there are no terms in second order with only one gradient. They disappear because of symmetry. Also note that this form of theory is in spirit completely equivalent to Ginzburg-Landau!

PROPERTIES FOR GRADIENTS.

It is easy to derive that we have the following relation for the gradients:

$$\langle \partial_a \delta X_i \frac{\partial \partial_b \delta X_j}{\partial t} \rangle = \langle \frac{\partial \partial_a \delta X_i}{\partial t} \partial_b \delta X_j \rangle \tag{6.68}$$

using the same reasoning as before. We also define the equivalent of the conjugate intensive fields in a similar manner as we derived for the fluctuations in the fields ϕ_i by

$$\mathcal{F}_{ia} = \sum_{jb} F_{iajb}\partial_b \delta X_j \tag{6.69}$$

and we have exactly as before

$$\langle \partial_a \delta X_i \mathcal{F}_{jb} \rangle = -k_B \delta_{ij}\delta_{ab} \tag{6.70}$$

ONSAGER'S THEOREM DERIVED.

We are almost ready to derive the Onsager relations. First of all, the rate of change in the gradient of an extensive quantity is proportional to the current density pertaining to that quantity:

$$\frac{\partial \partial_a \delta X_i}{\partial t} \propto \delta J_{ia} \tag{6.71}$$

which is easy to see, since doubling the current density will double the flow of material and hence double the change in gradient. Next, from our definition of the fields $\mathcal{F}$ we see that they behave like gradients of the intensive state variables. Since this is the only way we can define the conjugate fields for fluctuations, these are the fields that drive the currents. In the linear approximation we have therefore:

$$\delta J_{ia} = \sum_{jb} L_{iajb} \mathcal{F}_{jb} \tag{6.72}$$

in the same way as in the previous section. Taken together, we now have:

$$\frac{\partial \partial_a \delta X_i}{\partial t} = C \sum_{jb} L_{iajb} \mathcal{F}_{jb} \tag{6.73}$$

and hence

$$\langle (\partial_a \delta X_i)(\frac{d \partial_b \delta X_j}{dt}) \rangle = C \sum_{kc} L_{jbkc} \langle \partial_a \delta X_i \mathcal{F}_{kc} \rangle = -k_B L_{jbia} \tag{6.74}$$

Similarly we find

$$\langle \frac{\partial \partial_a \delta X_i}{\partial t} \partial_b \delta X_j \rangle = -k_B L_{iajb} \tag{6.75}$$

and hence

$$L_{iajb} = L_{jbia} \tag{6.76}$$

or

$$\mathcal{L}_{ik} = \mathcal{L}_{ki}^T \tag{6.77}$$

Therefore, the Onsager relations are a general consequence of the microscopic nature of matter, but we do not need to know any details. It is sufficient to know that the macroscopic laws are the limit of the microscopic description, and that the microscopic laws have time reversal symmetry. The form 6.66 for the fluctuations is simply the most general from we can write down in lowest order, and this form is sufficient for the purpose of proving Onsager's relations. The inclusion of magnetic fields is easy, we simply have to change the sign of all magnetic properties under time reversal. This gives some extra minus signs.

ENTROPY PRODUCTION.

In the previous section we derived the entropy production when currents are present in 6.40. When the currents are only due to fluctuations, this takes the form

$$P_s = \sum_{ia} \mathcal{F}_{ia} \cdot \delta J_{ia} \qquad (6.78)$$

or

$$P_s = \sum_{iajb} \mathcal{L}_{iajb} \mathcal{F}_{ia} \mathcal{F}_{jb} \qquad (6.79)$$

and this has to be positive, since entropy is always produced when there are fluctuations. Therefore, the eigenvalues of the tensor $\mathcal{L}$ have to be positive! Even though this statement follows from an analysis of fluctuations, if can now be generalized to all currents, since they have the same microscopic underpinning.

For example, consider the case where we only have a gradient in the chemical potential and only a flow of material. In that case we have $\vec{J}_N = L\vec{\nabla}\frac{-\mu}{T} = -\frac{L}{T}\vec{\nabla}\mu$ and because of the analysis above, L is positive. Therefore, the mass current is in the opposite direction of the gradient of the chemical potential, as is observed.

6.6 Thermo-electric effects.

TRANSPORT EQUATIONS FOR NQ SYSTEM.

We now apply the transport theory developed in the second section to a case where we have gradients in both the temperature and chemical potential. We have transport of material and energy, or in different words, transport of material and heat. Therefore we call this a NQ system. We repeat the equations for the currents and entropy production:

$$\vec{J}_S = \left(\frac{1}{T}\right)\vec{J}_U - \left(\frac{\mu}{T}\right)\vec{J}_N \qquad (6.80)$$

$$P_s = \left(\vec{\nabla}\left(\frac{1}{T}\right) \cdot \vec{J}_U - \vec{\nabla}\left(\frac{\mu}{T}\right) \cdot \vec{J}_N\right) \qquad (6.81)$$

The transport equations are in this case:

$$\vec{J}_U = \mathcal{L}_{UU} \cdot \vec{\nabla}\frac{1}{T} + \mathcal{L}_{UN} \cdot \vec{\nabla}\frac{-\mu}{T} \qquad (6.82)$$

and

$$\vec{J}_N = \mathcal{L}_{NU} \cdot \vec{\nabla}\frac{1}{T} + \mathcal{L}_{NN} \cdot \vec{\nabla}\frac{-\mu}{T} \qquad (6.83)$$

In many cases it is useful to replace the energy flow by the heat flow. because we have $\bar{d}Q = TdS$ we define

$$\vec{J}_Q = T\vec{J}_S = \vec{J}_U - \mu\vec{J}_N \tag{6.84}$$

which more or less states that the heat flow is the total flow of energy minus the flow of potential energy, represented by the last term in the equation above. Using the heat flow, we find:

$$P_s = \left(\vec{\nabla}\left(\frac{1}{T}\right) \cdot \vec{J}_Q + \frac{1}{T}\vec{\nabla}(-\mu) \cdot \vec{J}_N \right) \tag{6.85}$$

and

$$\vec{J}_Q = (\mathcal{L}_{UU} - \mu\mathcal{L}_{NU}) \cdot \vec{\nabla}\frac{1}{T} + (\mathcal{L}_{UN} - \mu\mathcal{L}_{NN}) \cdot \vec{\nabla}\frac{-\mu}{T} \tag{6.86}$$

or

$$\vec{J}_Q = (\mathcal{L}_{UU} - \mu\mathcal{L}_{NU} - \mu\mathcal{L}_{UN} + \mu^2\mathcal{L}_{NN}) \cdot \vec{\nabla}\frac{1}{T} - \frac{1}{T}(\mathcal{L}_{UN} - \mu\mathcal{L}_{NN}) \cdot \vec{\nabla}\mu \tag{6.87}$$

Similarly we have

$$\vec{J}_N = (\mathcal{L}_{NU} - \mu\mathcal{L}_{NN}) \cdot \vec{\nabla}\frac{1}{T} - \frac{1}{T}\mathcal{L}_{NN} \cdot \vec{\nabla}\mu \tag{6.88}$$

which can be written in the form

$$\vec{J}_N = \mathcal{L}_{11}\frac{1}{T} \cdot \vec{\nabla}(-\mu) + \mathcal{L}_{12} \cdot \vec{\nabla}\frac{1}{T} \tag{6.89}$$

$$\vec{J}_Q = \mathcal{L}_{21}\frac{1}{T} \cdot \vec{\nabla}(-\mu) + \mathcal{L}_{22} \cdot \vec{\nabla}\frac{1}{T} \tag{6.90}$$

with

$$\mathcal{L}_{11} = \mathcal{L}_{NN} = \mathcal{L}_{11}^T \tag{6.91}$$

$$\mathcal{L}_{12} = \mathcal{L}_{NU} - \mu\mathcal{L}_{NN} \tag{6.92}$$

$$\mathcal{L}_{21} = \mathcal{L}_{UN} - \mu\mathcal{L}_{NN} = \mathcal{L}_{12}^T \tag{6.93}$$

$$\mathcal{L}_{22} = \mathcal{L}_{UU} - \mu\mathcal{L}_{NU} - \mu\mathcal{L}_{UN} + \mu^2\mathcal{L}_{NN} = \mathcal{L}_{22}^T \tag{6.94}$$

These last equations can be written in the form of a similarity transformation:

$$\begin{pmatrix} \mathcal{L}_{11} & \mathcal{L}_{12} \\ \mathcal{L}_{21} & \mathcal{L}_{22} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ -\mu & 1 \end{pmatrix} \begin{pmatrix} \mathcal{L}_{NN} & \mathcal{L}_{NU} \\ \mathcal{L}_{UN} & \mathcal{L}_{UU} \end{pmatrix} \begin{pmatrix} 1 & -\mu \\ 0 & 1 \end{pmatrix} \tag{6.95}$$

which implies that the transformed tensor $\mathcal{L}_{ij}$ is also positive definite.

UNITS.

It is useful to take time to consider the dimensions of all quantities involved, and which units we are employing. In thermodynamics all material is counted in moles, not per particle. The transformation is easy, though, and involves Avogadro's number N_A. The current density in equation 6.82 is measured in $Jm^{-2}s^{-1}$, while the current density in 6.83 is measured in $Mm^{-2}s^{-1}$. The temperature is in K and the chemical potential is in JM^{-1}, where we use the symbol M for moles. From 6.82 we then find the following for the transport coefficients:

Coefficient	Dimensions
$\mathcal{L}_{UU}$	$JKm^{-1}s^{-1}$
$\mathcal{L}_{UN}$	$MKm^{-1}s^{-1}$
$\mathcal{L}_{NU}$	$MKm^{-1}s^{-1}$
$\mathcal{L}_{NN}$	$M^2J^{-1}Km^{-1}s^{-1}$

and similarly:

Coefficient	Dimensions
$\mathcal{L}_{22}$	$JKm^{-1}s^{-1}$
$\mathcal{L}_{21}$	$MKm^{-1}s^{-1}$
$\mathcal{L}_{12}$	$MKm^{-1}s^{-1}$
$\mathcal{L}_{11}$	$M^2J^{-1}Km^{-1}s^{-1}$

ELECTRICAL AND THERMAL CONDUCTIVITY.

For the rest of this chapter we confine ourselves to a specific case. Suppose we are describing the behavior of electrons in a metal. In that case the flow of material is equivalent to a flow of electrical current, and the heat flow is just the heat flow due to the electrons. Note that in any experiment we also have a heat flow due to the ions. This part of the heat flow has to be analyzed separately, and should not be included in the Onsager reciprocity relations! Basic quantities one defines are the electrical conductivity σ, which relates the electrical current density $\vec{j}$ to the electric field $\vec{E}$, and the thermal conductivity κ which relates the heat current density $\vec{J}_Q$ to the temperature gradient. The only contribution of interest to the chemical potential is the Coulomb potential, and we have:

$$\vec{j} = -N_A e \vec{J}_N \tag{6.96}$$

$$\vec{E} = \frac{1}{N_A e} \vec{\nabla} \mu \tag{6.97}$$

with $-e$ the charge of an electron. This gives

$$\vec{j} = \frac{N_A^2 e^2}{T} \mathcal{L}_{11} \cdot \vec{E} + \frac{N_A e}{T^2} \mathcal{L}_{12} \cdot \vec{\nabla} T \qquad (6.98)$$

$$\vec{J}_Q = -\frac{N_A e}{T} \mathcal{L}_{21} \cdot \vec{E} - \frac{1}{T^2} \mathcal{L}_{22} \cdot \vec{\nabla} T \qquad (6.99)$$

where the parameters $\mathcal{L}_{ij}$ only account for the effects of the electrons.

The entropy production expressed in these quantities is:

$$P_s = -\frac{1}{T^2} \vec{\nabla} T \cdot \vec{J}_Q + \frac{1}{T} \vec{E} \cdot \vec{j} \qquad (6.100)$$

Since the heat production is TP_s we see immediately that the second term is the standard heat production as described in electricity theory. The first term is the heat produced when a heat flow goes to a lower temperature.

The electrical conductivity tensor σ is defined at constant temperature by $\vec{j} = \sigma \cdot \vec{E}$, $\vec{\nabla} T = 0$, and this gives

$$\sigma = \frac{N_A^2 e^2}{T} \mathcal{L}_{11} \qquad (6.101)$$

and has dimensions $C^2 N^{-1} m^{-2} s^{-1}$ as needed. Remember that the electric field has dimensions NC^{-1}. Also, because of the Onsager relation we have that $\sigma = \sigma^T$.

The thermal conductivity tensor κ for the electrons is defined by the heat current due to the electrons as a function of the thermal gradient, when there is no electrical current, or $\vec{J}_Q = -\kappa \cdot \vec{\nabla} T$, $\vec{j} = 0$. Because there is no electric current there is an electric field counteracting the force due to the thermal gradient:

$$0 = \frac{N_A^2 e^2}{T} \mathcal{L}_{11} \cdot \vec{E} + \frac{N_A e}{T^2} \mathcal{L}_{12} \cdot \vec{\nabla} T \qquad (6.102)$$

or

$$\vec{E} = -\frac{1}{N_A e T} \mathcal{L}_{11}^{-1} \mathcal{L}_{12} \cdot \vec{\nabla} T \qquad (6.103)$$

and hence

$$\vec{J}_Q = \frac{1}{T^2} (\mathcal{L}_{21} \cdot \mathcal{L}_{11}^{-1} \mathcal{L}_{12} \cdot \vec{\nabla} T - \mathcal{L}_{22} \cdot \vec{\nabla} T) \qquad (6.104)$$

which gives

$$\kappa = \frac{1}{T^2} (\mathcal{L}_{22} - \mathcal{L}_{21} \mathcal{L}_{11}^{-1} \mathcal{L}_{12}) \qquad (6.105)$$

and again because of Onsager we have $\kappa = \kappa^T$.

CUBIC MATERIALS ARE EASY.

In cubic materials all tensors in Carthesian space are simple numbers times the unit matrix. Therefore, we have only three numbers that characterize the transport, L_{11}, $L_{12} = L_{21}$, and L_{22}. In that case the electrical and thermal conductivity are given by:

$$\sigma = \frac{N_A^2 e^2}{T} L_{11} \tag{6.106}$$

$$\kappa = \frac{1}{T^2}(L_{22} - L_{21}^2 L_{11}^{-1}) \tag{6.107}$$

and we have

$$\sigma\kappa = \frac{N_A^2 e^2}{T^3}(L_{11}L_{22} - L_{21}^2) \tag{6.108}$$

and since the matrix of transport coefficients is positive definite, we see that in this case:

$$\sigma\kappa > 0 \tag{6.109}$$

which, of course, can be easily generalized, and holds in all cases, when we interpret the greater than to mean being positive definite. This relation is no surprise, since electrical currents always follow the electric field, and thermal currents always follow the inverse temperature gradient. But here we have related these common observations to the production of entropy, which gives the fact that the matrix of transport coefficients is positive definite. The electrical conductivity is positive because of Newton's law. The thermal conductivity is positive because of the second law of thermodynamics.

THERMOPOWER.

Equation 6.102 has interesting consequences. If there is a temperature gradient across a conductor, and if the end points are not connected and no current can flow, there will be a particle flow inside the material causing a buildup of charge at the endpoints. The particle flow will stop when the electric force balances the thermal force, and the resultant electric field follows from 6.102, as given before:

$$\vec{E} = -\frac{1}{N_A eT} \mathcal{L}_{11}^{-1} \mathcal{L}_{12} \cdot \vec{\nabla} T \tag{6.110}$$

The constant of proportionality is the <u>absolute thermoelectric power</u> tensor ϵ, defined by $\vec{E} = \epsilon \vec{\nabla} T$, and it follows that

$$\epsilon = -\frac{1}{N_A eT} \mathcal{L}_{11}^{-1} \mathcal{L}_{12} \tag{6.111}$$

Note that the nature of the charge carriers is reflected in the sign of ϵ. The carrier concentration will be less at higher temperatures. Therefore, if the charge

carriers are positive, the low temperature part will have a larger positive charge, and the resulting field will be towards the high temperature. For negative charged carriers this is the opposite.

Suppose we have a material with end points at temperatures T_1 and T_2. No current flows, and therefore the difference in potential between the end points is

$$V_2 - V_1 = -\int_1^2 \vec{E} \cdot d\vec{r} = -\int_1^2 d\vec{r} \cdot \epsilon \cdot \vec{\nabla} T \tag{6.112}$$

If we now take two different materials and connect the end points at one end, there will be a potential difference between the unconnected end points at the other end. The larger the difference in thermoelectric power between the two materials, the larger the voltage difference.

A very simple expression can be obtained if we assume that the temperatures are very close together, and the material is cubic. Then we have

$$V_2 - V_1 \approx (T_1 - T_2)\epsilon \tag{6.113}$$

where the tensor is now reduced to a number times the unit matrix. If we measure the voltage difference at the disconnected end points at T_1 we find:

$$V_1^x - V_1^y \approx (T_1 - T_2)(\epsilon^y - \epsilon^x) \tag{6.114}$$

which shows how a thermocouple can be used to measure a temperature difference.

If we compare with formula 6.3 we see that:

$$\alpha_{AB} = \epsilon^A - \epsilon^B \tag{6.115}$$

REFORMULATION OF THE TRANSPORT EQUATIONS.

The equations for the electric and heat current densities can now be modified by eliminating the transport coefficients in terms of the measurable quantities we used in the previous subsections. We obtain:

$$\mathcal{L}_{11} = \frac{T}{N_A^2 e^2} \sigma \tag{6.116}$$

$$\mathcal{L}_{12} = -N_A e T \mathcal{L}_{11} \cdot \epsilon = -\frac{T^2}{N_A e} \sigma \epsilon \tag{6.117}$$

$$\mathcal{L}_{21} = \mathcal{L}_{12}^T = -\frac{T^2}{N_A e} \epsilon^T \sigma^T \tag{6.118}$$

$$\mathcal{L}_{22} = T^2 \kappa + T^3 \epsilon^T \sigma^T \epsilon \tag{6.119}$$

which yields the following equations:

$$\vec{j} = \sigma \cdot \vec{E} - \sigma \epsilon \vec{\nabla} T \qquad (6.120)$$

$$\vec{J_Q} = T \epsilon^T \sigma \vec{E} - (\kappa + T \epsilon^T \sigma \epsilon) \vec{\nabla} T \qquad (6.121)$$

OTHER THERMOELECTRIC EFFECTS.

When a current flows through a material at constant temperature, it causes an electric field across the material, which in turn causes a heat flow. In this scenario we have

$$\vec{J_Q} = T \epsilon^T \vec{j} \qquad (6.122)$$

for $\vec{\nabla} T = 0$. If we force a current through two different materials connected in series, the heat flow will be different in the two materials. Therefore, at the junction heat is produced or absorbed. The amount is

$$\Delta Q = T \Delta \epsilon^T \vec{j} \qquad (6.123)$$

This is the <u>Peltier effect</u>. By comparing with equation 6.4 we see that

$$\Pi_{AB} = T \Delta \epsilon \qquad (6.124)$$

for cubic materials, which is the relation found by Kelvin in an empirical manner.

HEAT GENERATION IN RESISTORS.

We all know the formula for the generation of heat in a resistor, where power production is proportional to $\vec{j} \cdot \vec{E}$. This formula, however, assumes constant temperature. What if there is also a temperature gradient in the resistor? We can find the answer quite easily. Assume that we drive a current density $\vec{j}$ through a resistor, and that there is a temperature gradient $\vec{\nabla} T$. These two quantities determine completely the state of the system, because of the transport equations. The electric field in the resistor follows from 6.120:

$$\vec{E} = \rho \cdot \vec{j} + \epsilon \vec{\nabla} T \qquad (6.125)$$

where ρ is the resistivity tensor, the inverse of the conductivity tensor. The electric field is caused by both a charge transport due to the applied current and a charge transport due to the thermal gradient. The heat current follows from 6.121 and is

$$\vec{J_Q} = T \epsilon^T (\vec{j} + \sigma \epsilon \vec{\nabla} T) - (\kappa + T \epsilon^T \sigma \epsilon) \vec{\nabla} T = T \epsilon^T \vec{j} - \kappa \vec{\nabla} T \qquad (6.126)$$

The entropy production follows from 6.100:

$$P_s = -\frac{1}{T^2}\vec{\nabla}T \cdot (T\epsilon^T\vec{j} - \kappa\vec{\nabla}T) + \frac{1}{T}(\rho \cdot \vec{j} + \epsilon\vec{\nabla}T) \cdot \vec{j} \qquad (6.127)$$

which leads to production of thermal energy at a rate

$$P = TP_s = \vec{j} \cdot \rho \cdot \vec{j} + \frac{1}{T}\vec{\nabla}T \cdot \kappa \cdot \vec{\nabla}T \qquad (6.128)$$

as expected. The first term is the Joule heat, the second term the heat generated while keeping a temperature gradient.

Now we will perform a different experiment. We set up a resistor and fix the temperatures at the end points, under conditions where there is no electric current. This sets up a heat flow in the resistor, and sets up a temperature profile in the resistor. Since heat is flowing, and heat is generated, the temperature profile would change unless we keep each point in contact with a heat reservoir. This is exactly what we do in the following experiment. We take a conductor, and at each point of the conductor we make thermal contact with a reservoir, in such a manner that the temperature of the conductor at each point remains at a constant value. Because of the generation of heat and the heat currents, this means that at each point of the conductor there is a heat flow into or out of the reservoir, needed to keep the temperature at that point constant.

We now ask the following question. In the previous set-up, if we now add an electric current in the conductor, what is the **additional** heat flow into or out of the reservoir needed to keep the temperature the same? In order to calculate this, we need to calculate the change in internal energy at each point.

The energy transport is given by $\vec{J}_U = \vec{J}_Q + \mu\vec{J}_N$ and the local change in energy follows from

$$\frac{\partial u}{\partial t} = -\vec{\nabla} \cdot \vec{J}_U \qquad (6.129)$$

In a steady state there is a constant profile in the particle density (no accumulation of charge!), and we have

$$0 = \frac{\partial n}{\partial t} = -\vec{\nabla} \cdot \vec{J}_N \qquad (6.130)$$

and hence

$$\frac{\partial u}{\partial t} = -\vec{\nabla} \cdot \vec{J}_U = -\vec{\nabla} \cdot \vec{J}_Q - (\vec{\nabla}\mu)\vec{J}_N = -\vec{\nabla} \cdot \vec{J}_Q + \vec{E} \cdot \vec{j} \qquad (6.131)$$

Using equations 6.125 and 6.126 we get

$$\frac{\partial u}{\partial t} = -\vec{\nabla} \cdot (T\epsilon^T\vec{j} - \kappa\vec{\nabla}T) + (\rho \cdot \vec{j} + \epsilon\vec{\nabla}T) \cdot \vec{j} \qquad (6.132)$$

and since $\vec{\nabla} \cdot \vec{j} = 0$ this leads to

$$\frac{\partial u}{\partial t} = \vec{j} \cdot \rho \cdot \vec{j} + \vec{\nabla} \cdot (\kappa\vec{\nabla}T) - T(\vec{\nabla}\epsilon^T) \cdot \vec{j} \qquad (6.133)$$

and since the thermopower only changes because the temperature changes we write this in the form

$$\frac{\partial u}{\partial t} = \vec{j} \cdot \rho \cdot \vec{j} + \vec{\nabla} \cdot (\kappa \vec{\nabla} T) - T(\vec{\nabla} T) \cdot \frac{d\epsilon^T}{dT} \cdot \vec{j} \tag{6.134}$$

Suppose there is no current. Than the change in internal energy is given by

$$\frac{\partial u_0}{\partial t} = \vec{\nabla} \cdot (\kappa \vec{\nabla} T) \tag{6.135}$$

and this determines the heat flow with the reservoir at each point. When there is a current, the **additional** heat flow is therefore:

$$\frac{\partial u_j}{\partial t} = \vec{j} \cdot \rho \cdot \vec{j} - T(\vec{\nabla} T) \cdot \frac{d\epsilon^T}{dT} \cdot \vec{j} \tag{6.136}$$

The first term is easy, and is the Joule heat generated in each point in the conductor. In order for the conductor to remain at a constant temperature profile this Joule heat needs to go into the reservoir. The second term is a new heat source, and this is called the <u>Thomson heat</u>. It is linear in both the thermal gradient and the electric current and for small currents dominates the Joule heat! The strength of this heat source is directly related to the temperature derivative of the thermo-power.

Comparing with equation 6.6 we see that

$$\tau = T \frac{d\epsilon}{dT} \tag{6.137}$$

for cubic materials, again in agreement with what Kelvin found empirically.

What happened to the minus sign when we went to the equation above?

ADIABATIC CONDUCTIVITY.

A recurring theme in thermodynamics is that the values of measured properties depend on the conditions under which experiments are performed. If we measure the conductivity of a material at constant temperature we find the property σ. It is also possible to perform the experiment under adiabatic conditions, in this case demanding that $\vec{J}_Q = 0$. Equation 6.121 then gives

$$T\epsilon^T \sigma \vec{E} = (\kappa + T\epsilon^T \sigma \epsilon)\vec{\nabla} T \tag{6.138}$$

and equation 6.120 then leads to

$$\vec{j} = \sigma \cdot \vec{E} - \sigma\epsilon(\kappa + T\epsilon^T \sigma \epsilon)^{-1} T\epsilon^T \sigma \vec{E} \tag{6.139}$$

and hence the adiabatic conductivity is given by

$$\sigma_{ad} = \sigma(1 - \epsilon(\kappa + T\epsilon^T\sigma\epsilon)^{-1}T\epsilon^T\sigma) \tag{6.140}$$

As always, we need to define which are the state variables we have under control. Note that for very large temperatures the adiabatic conductivity goes to zero!

What does it mean that the adiabatic conductivity is zero?

EXTERNAL VERSUS TOTAL CHEMICAL POTENTIAL.

We related the gradient in the chemical potential to the electric field by

$$\vec{E} = \frac{1}{N_A e}\vec{\nabla}\mu \tag{6.141}$$

but this is obviously only the gradient of the external chemical potential. We also know from thermodynamics that

$$SdT - Vdp + Nd\mu = 0 \tag{6.142}$$

and since we assume that the pressure is always zero we set $dp = 0$. Therefore we have for the gradients:

$$S\vec{\nabla}T + N\vec{\nabla}\mu_{tot} = 0 \tag{6.143}$$

or

$$S\vec{\nabla}T + NN_A e\vec{E} + N\vec{\nabla}\mu_{int} = 0 \tag{6.144}$$

Therefore, if we apply an electric field and a temperature gradient, we automatically generate a gradient in the internal chemical potential, and hence a gradient in the amount of material! This is a warning sign when we want to compare thermodynamics and microscopic calculations. A similar situation occurs in dielectrics, where on a microscopic level we calculate the response of the system to a change in the total field, including the induced dipole field, driven by an applied field. In our case, a microscopic calculation would give results of the form

$$\vec{j}_N = \mathcal{R}int \cdot \vec{\nabla}\mu_{int} + \mathcal{R}ext \cdot \vec{\nabla}\mu_{ext} + \mathcal{R}_T\vec{\nabla}T \tag{6.145}$$

We then use the relation 6.144 to distribute the effects of the internal chemical potential over the gradient contributions for temperature and applied field in order to get the response functions needed in thermodynamics.

Appendix A

Questions submitted by students.

Students were asked to submit 10 question they would like to see included in the notes, similar to the questions already included, shown in italics. Errors are due to my editing. Some questions were left out because of duplication.

A.1 Questions for chapter 1.

- What is the high temperature reservoir for an internal combustion engine?

- Are the relations $\frac{T}{T_0} = 1 - \eta_C$ assured, derived, or observed?

- Is there a standard or limit to which real gases can follow the ideal gas approximations?

- The energy of an ideal gas is $\frac{D}{2}NRT$, where D is the number of dimensions? Why is there a factor one-half for each dimension?

- Is there an extensive variable that we have not yet figured out how to measure, and how will this ignorance affect existing laws?

- Work can be done in many different ways. Do different mechanisms for heat transfer lead to different TdS values?

- Our bodies have more or less the same temperature, but do give of different amounts of heat. Can this be used to calculate the disorder in our bodies and predict human defects?

- In a system that is not in equilibrium, what can we say about deterministic behavior?

- Do we have the same thermodynamic laws on the moon?

- Are the laws of thermodynamics valid in accelerated systems?

- Does the second law of thermodynamics hold for our mind? Could we create more than we have learned?

- Is it always possible to find other reversible processes that have the same initial and final state?

- The third law states that $\lim_{T\to 0} S(T) = 0$, but does this not lead to contradictions when we also have $\Delta S = \frac{\Delta Q}{T}$?

- How can we explain the second law of thermodynamics when an electric field acts on a dielectric and rearranges the dipoles?

- Is the third law derived from experimental observations?

- What would our world look like at T=0?

- Are state variables always dependent on other state variables?

- Give an example of a system that can be made to be in thermodynamic equilibrium

- Are there systems that are not in equilibrium but that can be modelled using thermodynamic equilibrium assumptions?

- What would be a consequence of the zeroth law being wrong?

- Are there easy relations for exact differentials when we have more than two variables? E.g. when is $\bar{d}g = h(x,y,z)dx + k(x,y,z)dy + j(x,y,z)dz$ exact?

- What is the importance of reversibility?

- Can the efficiency be exactly zero?

- If entropy change is irreversible, what does that imply for the fate of the universe?

- If in the equation $\lim_{N\to\infty} \lim_{T\to 0} S = 0$ we could interchange the limits, what would the consequences be?

- How would things change if entropy was reversible?

- Give some examples of reversible processes

- Give some examples of irreversible processes

- Give some examples of other extensive thermodynamic variables

- Give some examples of other intensive thermodynamic variables

- Find the exact differential df for $f(x, y) = 3x^y - 6yx^2$ and $y = y(u, v)$

- What are the consequences of having a Carnot engine with $\eta > 1$?

- What are the consequences of having a Carnot engine with $\eta < 0$?

- What happens to the efficiency of a Carnot engine when T_1 is finite and $T_2 \to 0$?

- If the entropy of the universe is always increasing, is the universe a reversible process?

- Why can't we measure entropy directly?

- How do you know when you have enough state variables?

- Why does a process have to be reversible in order to study it in thermodynamics?

- Why are the laws of thermodynamics numbered 0 to 3 and not 1 to 4?

- In defining heat and work flow, which sign convention do you prefer and why?

- How would you state the second law?

- Why does the cycle used in the Carnot cycle produce the most efficient engine?

- Why would you ever use a less efficient engine?

- Why will a completely isolated system end up in equilibrium?

- Why can't we reach zero temperature?

- If you would be designing a temperature scale, what would you base it on and why?

- The universe is cooling down; can it reach zero temperature?

- Is the big bang a reversible process?

- Why would someone want to study macroscopic systems?

- Are there any state variables describing a piece of iron that we have not yet mentioned?

- Give examples of state functions

- Give an example of a spontaneous process

- What is the difference between Kelvin's and Clausius' statements of the second law?

- Why is temperature considered a state variable, but heat not?

- Why can't we measure temperature directly?

- Why does the error in the integration when adding many Carnot cycles to describe an arbitrary process approach zero when $\Delta T \to 0$ for each cycle?

- Why is the TdS term necessary in the first law?

- Why does the entropy increase when a system reaches equilibrium in a spontaneous process?

- What is a system?

- How can you tell the state a system is in?

- Is the natural evaporation/rain cycle an engine?

- Does heat flow?

- Why is the combination of an electric motor and generator not capable of being more efficient than a Carnot engine?

- What makes an engine less efficient than a Carnot engine?

- Considering the example of combining two Carnot engines to get a Carnot engine operating between arbitrary temperatures, does this show that temperature is a state variable?

- Are there consequences to the universe from the inequality of irreversible processes?

- Does the maximization of entropy have any universal consequences?

- How does the statement $\lim_{T \to 0} \left(\frac{\partial U}{\partial T} \right)_{V,N} = 0$ about the limit of the partial derivative agree/disagree with the quantum mechanical statement that the energy of an oscillator is never at the bottom of the well?

A.2   Questions for chapter 2.

- Why is the minimum energy principle important?

- What is the usefulness of writing all of these free energies in differential form?

- How many Maxwell relations can there be?

- Why are response functions used in experiment?

- If your finger had a small heat capacity, does this mean your finger would burn less if you touched a hot stove?

- What is the usefulness of writing S as a function of T, V, and X?

- If the compressibility at constant entropy was less than zero, what consequences would this have on engines?

- Based on physical grounds, why is the product in 2.100 less than or equal to 0?

- What are the possible uses of the magnetic susceptibility at constant temperature and the magnetic susceptibility at constant entropy?

- What would be some of the effects on closed systems if the expectation value of the product of delta U and delta N was zero.

- In the third case in the beginning of chapter 2,how can we be sure that the equilibrium that has been reached by suspending the mass is the same equilibrium without it?

- Why we can choose all the independent variables to be extensive?

- What is more fundamental in Maxwell relations?Is it the mathematical rules or the physical relations?

- Are equations 2.30 and 2.31 valid for irreversible process?

- Explain the three lines after 2.37 about compressibility?

- Prove equation 2.51?

- How can we explain in physical words equation 2.83 which relates different response functions?

- How our analysis of a magnetic system will change if we have a nonlinear magnetic response (ferromagnetic material)?

- How can we include the higher order susceptibilities in our analysis?

- Is it possible to determine ω in equation 2.135 by macroscopic analysis only?

- Is the correlation between fluctuation in U and N trivial (reasonable)?

- Are all free energies a minimum of their internal degrees of freedom when in equilibrium?

- Why are the extensive entropy second derivatives related to a no-root condition?

- Does the value $-\frac{V}{4p}$ in 2.127 have any special significance?

- Why are the quantities in 2.135 a Gaussian?

- Why does the exponent in 2.139 contain a factor of $\frac{1}{2}$?

- Should the fluctuations going to zero in the thermodynamic limit surprise you?

- Is the correlation of the fluctuations a consequence of the uncertainty principle or does it represent a more general uncertainty relationship?

- When will the partial derivatives cancel in a special way and why?

- Why do the derivative permutations change sign?

- In a non-equilibrium condition is it possible to have a negative heat capacity and what would it mean?

- Since there are several different ways to write the energy in thermodynamics, is there something fundamentally missing from thermodynamics that is not missing from classical mechanics?

- We have these things called Maxwell Relations for different thermodynamics variables. Can we formulate such relations for other disciplines?

- When doing flow in magnetics, or other solid state phenomenological processes, we run into vortices. These seem to be a special form of fluctuations. Are they?

- What are the implications to the theory if we were ever to find a negative compressibility or heat capacity.

- Can we really make a closed system, and why would we want to, since we can't interact with it.

- Most of the inconsistencies in thermodynamics can be ironed out with quantum mechanics, but the first uses of thermodynamics were well before quantum mechanics, how did those scientists work out the problems?

- With the three systems that we discussed early in the chapter, only one was experimental, but all three were different, why?

- Can you derive a general form of the Maxwell relations that we can then just plug the different variables into?

- Why do we rely so much on the ideal gas law when it only works in equilibrium, and most systems we study are not in equilibrium?

- How difficult is it to find Maxwell relations for more than two variables?

- How can a system exchange heat with the outside world, yet remain at constant entropy?

- Why are the $SdT - Vdp + Nd\mu + Xdx$ terms not stated when expressing dU?

- In equation 2.65 is $\left(\frac{\partial U}{\partial S}\right)_{V,N,X} = \left(\frac{\partial U}{\partial S_l}\right)_{V,N,X} = T_l$?

- What is the general rule for figuring out where the minus signs come in when taking products of partial derivatives of many variables.

- Does the relation $\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}$ hold at very low temperatures?

- Why are all the other intensive-extensive variable pairs called work yet the temperature - entropy pair referred to as heat exchange.

- For the inequality derived before 2.74, of the form $ax^2 + bx + c \geq 0$, would imaginary roots have any physical meaning?

- Can we say anything about the value of μ in the limit $\frac{N}{V} \to 0$?

- What is energy?

- How can you tell which thermodynamic potential is appropriate?

- In the first case (no friction) on page 41, how long will the oscillations last? Why?

- Why is heat always generated in an irreversible process?

- Why are Legendre transformations useful?

- Prove that the Gibbs potential is a state function and that its differential is exact.

- How did the grand potential get its name?

A.3   Questions for chapter 3.

- Is energy the only factor to determine the phase state, what about other quantum factors?

- How many phase transitions do we have?

- Can the special relativity and time play any role here?

- Why is figure 3.13 impossible?

- Can we give the phase transition an analysis based on chaos?

- For the van der Waals equation, if b=0 and T=an/R then p=0, why?

- Why does the integral 3.31 yield A1-A2 ?

- How will the van der Waals equation be changed if we include magnetization?

- Do we have any universal constants associated with the van der Waals equation?

- Why is the volume of the ice bigger than that of water?

- Are there any materials where the phase boundary for solid to liquid has a negative slope?

- Are there other systems where the energy of interest is not the Gibbs energy?

- Why does the phase transition in Gibbs free energy always jump down?

- Using stability and the model phase diagram in $p - V$ space, can you explain why the triple point is where it is?

- If we made a three dimensional graph of G(p,T) for 2 phases what would we see?

- Can the Van Der Waals equation be derived from a virial expansion?

- Why look at the asymptotic forms?

- What do negative pressures in the Van Der Waals equation mean?

- How important is scaling?

- Why does crossing a phase boundary cause a jump in the value of the volume?

- Do you think that the phase boundary between solid and liquid will vanish if we can reach a high enough pressure?

- Why is it often better to go around the critical point instead of crossing through the phase boundary?

- Why do inaccessible regions only show up in phase diagrams when extensive variables are involved?

- Is there anything besides the indices of refraction that we can use to distinguish a liquid from a gas?

- How are the forbidden regions of a V-T diagram related to the corresponding p-T graph?

- Why do systems in forbidden regions phase separate?

- Why is the eutectic point important?

- Why are phase transitions important to thermodynamics?

- Why is it important to include entropy as one of the state variables in our model system?

- What importance does the triple point have in industry?

- How would we find V_c and T_c for water?

- Why do we need weights in the equation $\sum w_i N_i = N$ on page 102?

- Why are there regions in which the $c_B T$ diagram which are not allowed?

- Why is the ideal gas law an approximation?

- Why are some of the intermediate states unstable?

- What is the difference between mechanically stable and thermodynamically stable states?

- Can water be heated over 100 degrees Celsius?

- For p-V-T systems not in equilibrium, why can equations of state like p=f(V,T) not exist?

- In the p-T diagram for solid Ce in 3.2 with axis interchanged, does the fact that this curve is not concave downwards contradict the 'consequences for second order derivatives' discussed in chapter 2?

- Where would a plasma 'fit in' on a phase diagram like fig 3.1?

- If a system were prepared at a given Magnetization M_0 at high temperature and then cooled to a temperature which will force the state of the system into an inaccessible region, will the system phase separate?

- If so, will the magnetization be in different directions, have different magnitudes, or both.

- In a system with 4 independent state variables, what is the maximum number of phases that can coexist?

- We see that negative pressures are allowed by the Van der Waals equation of state. Are negative temperatures also allowed?

- During the binodal decomposition, why are time scales important?

- In trying to achieve stability, does a system necessarily become mechanically stable first, then thermodynamically stable, or can these two processes occur simultaneously, incrementally.

- Various groups of materials have common molecular sizes, interaction energies etc. within their groups. Are there various, commonly used, virial expansions for each such group?

- When mixing two materials, we get a binary phase diagram. What would the diagram look like if we were to mix three or more materials?

- Why use the van der Waals equation of state when it is limited in the systems that it can describe?

- Are there systems with only meta-stable states?

- Theoretically, we can have negative pressure, why can't we measure it?

- Can we make a material that exists in an unstable region, but will not easily break down?

- Why doesn't negative pressure correspond to a physical state?

- When are non-unique energy solutions better at describing a system?

- Can pressure be multi-valued for a single temperature?

- Can temperature be multi-valued for single values of volume?

- Can volume be multi-valued for single values of temperature?

A.4   Questions for chapter 4.

- Is there really no long-range order in a liquid?

- Can we have spontaneous broken symmetries in a non-degenerate system?

- Landau's theory does not converge at Tc, but can't we modify the theory so that it does converge?

- Can there be third order phase transitions, or is that forbidden by the free parameters?

- Can both heat capacities be modelled by the same response?

- What happens when there is a positive term in the fourth order sign of the expansion?

- Is there a place where all three roots will have the same value of f for the same m?

- Can we make our expansions work to get rid of anisotropies in the system?

- How important are inhomogeneities in a system?

- If the correlation length diverges at Tc, why is it so important in the theory?

- Why do we need a non-equilibrium theory to describe the effects of fluctuations in a system?

- How is snow different from ice?

- Why must an order parameter be extensive?

- Why do we measure the values of an order parameter via the associated generalized force instead of measuring it directly?

- Why do we compare free energies to determine if the state is an equilibrium state?

- Prove that there are no singularities in state functions for finite systems.

- Where do you see hysteresis in E-and-M?

- Why are there large fluctuations in the order parameter near the phase transition?

- Why is it so hard to describe the system at the critical temp?

- Why do small changes affect the whole system at the critical temp?

- Can we describe phase transition by complex functions?

- Can we describe phase transition by group theory?

- What is the effect of pressure on Landau form of free energy?

- Is Landau theory equivalent to a unified theory in particle physics?

- Is there any theory that describes exactly what's happening at a phase transition?

- Is it possible to define b(T) in such away to have the correct exponent in (4.12)?

- What's the meaning of nucleation and growth?

- Do you know any real system with first order transition?

- Is the description for fluctuations for macroscopic systems related to the uncertainty principle for microscopic systems?

- Is the correlation length related to the susceptibility?

- By what mechanism does a tap on a beaker of supercooled water cause it to suddenly crystalize?

- Is it possible to apply our external field over such a large time scale that we can ignore fluctuations even near a phase transition?

- Can we use Cauchy's 1st theorem to evaluate our Landau function at the critical point?

- Is our "Divide and conquer" technique for considering fluctuations analogous to our "equivalent surface and volume charges" for considering dielectric samples?

- What physical consequences would there be if our "f" in eq'n 4.37 were negative, ie. fluctuations lowered our energy state?

- What is our sigma*dm equivalent to supercooling and superconductivity?

- Would analytic continuation help the evaluation of our Landau expansion at the critical point?

- For the change in local magnetic field causing a perturbation in the magnetization everywhere; does this perturbation happen instantaneously or does it travel at the speed of light?

- Does causality play a role in this perturbation?

- At r=0 it is reasonable to speak of E=-gradient(Potential), why then is an expansion of free energy in terms of gradients of the order parameter not valid near Tc.

- Why do experiments give different results than the Van Der Waals model at the phase transition?

- What would be a suitable order parameter for describing the phase transition between snow and ice?

- Why is it important to compare the idea of a critical point in thermodynamics to the idea of a critical point in mathematics?

- What kind of expansion would be needed to describe f exactly?

- Would this analysis be appropriate for approximating the nature of a bar magnet?

- Is the transition from liquid water to ice a second or first order phase transition?

- At which point on the hysteresis will a butterfly flapping its wings 1000 miles away cause the system to go from a meta-stable state to a stable state?

- What mathematical operations were used to derive (4.38)?

- Why does rotational symmetry cause the solutions to be of the form $u_l(r)Y_lm(\omega)/r$?

- What parameters would tell us whether a system is ice or snow?

A.5   Questions for chapter 5.

- Why in deriving the pair correlation function we assume a spherical symmetry?

- Can we replace h and n by one critical exponent?

- Is the law described by the correlation function obeying the third Newton law?

- What is the physical meaning of the fact that the susceptibility is proportional to the q=0 component of the Fourier transform of the pair correlation function?

- Are in reality the dependence of the response functions with respect to T is the same above and below the critical temperature

- What is the critical field?

- Is there a mean field theory associated with the first phase transition?

- How can we be sure that it is enough to treat the system near the critical temperature in a perturbation theory?

- How can Ginzburg Landau theory give valid measurements while wrong critical exponents?

- What is the maximum number of critical exponents?

- The critical exponents shown have simple relations to T and Tc. How can this be possible, when we know a state is dependent on at least two variables.

- I have seen the reduced p,T,V written as t=T/Tc, etc. We do not do that in this chapter. Which is the correct version.

- Since statistical mechanics can get us to the heart of phase transitions, why bother doing this with thermodynamics.

- How many other critical exponents are there.

- Is there a simpler way to find our descriptions other than scaling.

- How do we relate the functionals that come out of scaling to experimental data.

- Critical exponents can be hard to get out of state equations, and they do not seem to give any new information. Why use them.

- How can critical exponents get you back to the phase diagram. I just don't see the connection.

- If the exponents are the same for T¿Tc or T¡Tc, why do we bother to define them separately.

- Which is the most powerful and useful critical exponent.

- Why would gamma not equal gamma prime?

- What would happen if Tc and pc could be negative?

- Why must delta M ¡¡ M?

- How can you have a 2 dimensional system?

- Why must a realistic description of a phase transition near a critical point include the effects of fluctuations?

- Why does the correlation length become very large near a critical point?

- Where else do we see scaling and universality?

- Why are critical exponents so difficult to measure?

- How can you measure a pair correlation function?

- Why can we use any function of two variables as a basis for scaling?

- Why do fluctuations occur near the critical point?

- Would an engineer want to know the critical exponents of a steam engine?

- Why is it important to know the mean field approach?

- What is the usefulness of using relative variables?

- Is the scaling function a mathematical convenience or does it have physical significance?

- If critical exponents are so hard to measure, what is their usefulness?

- Could we have described the change in magnetization over time by something other than the diffusion equation?

- Would it be plausible to use a relativistic form of the equations?

- Why does the scaling theory give nu=nu'?

- What would happen if we used the compressibility as the response function?

Appendix B

Summaries submitted by students.

Students were asked to submit a paragraph describing each chapter, written in a way they would like to see it included in an introductory description of the notes. Therefore these paragraphs reflect both the understanding of the material and the exposition of the material.

B.1 Summaries for chapter 1.

In thermodynamics one describes a macroscopic system, with many degrees of freedom, by state variables (which are time-averaged). For state variables to be useful in predicting intermediate values, thermodynamics concerns itself only with reversible processes in thermodynamic equilibrium in the thermodynamic limit. State variables are governed by the laws of thermodynamics. Laws zero and three give us fixed references. Law one is the conservation of energy and law two tells us that if all the processes are reversible we have the best scenario, otherwise entropy increases.

Thermodynamics is the study of macroscopic systems in equilibrium. We use thermodynamics to help define experimental variables such as temperature and pressure. Using thermodynamics we can set up simple experiments to test our theories, and we can use our experimental results to find simple relationships for our variables.

Chapter 1 introduces extensive and intensive thermodynamical variables, talks about what they mean, talks about reversibility and irreversibility, and how quasi-static systems work in thermodynamics. Chapter 1 also goes over the four laws of thermodynamics, and introduces some mathematical formalism. The end of chapter 1 talks about entropy in the context of the third law. There are

also definitions of what we mean by macroscopic systems, state, thermodynamic equilibrium, and other thermodynamic vocabulary terms.

Rules, rules, rules. Everything in life seems to be governed by rules. The best way to understand any system, from a society to a steam engine, is by looking at the laws that govern its behavior. In this chapter we will learn the language of thermodynamics and study the laws that apply to thermodynamic systems. The first law included heat as a form of energy and states that the total energy of a system is conserved. The second law puts restrictions on the transfer of heat or the exchange of heat into work. It defines a preferred direction of time and tells us that no engine can be more efficient than a Carnot engine. The third law says that, in the thermodynamic limit, when the temperature goes to zero so does the entropy. It is thus impossible to reach T=0K using a reversible process in a finite number of steps. Finally, the zeroth law, which is so trivial it is often overlooked, states that if two systems are in equilibrium with the same system, they are also in equilibrium with each other. This simple fact is what allows us to define universal standards for temperature, pressure, and all the other descriptors of our system. With these laws in hand we can begin to understand the behavior of thermodynamic systems throughout the land.

This chapter will quickly review the 4 basic laws of thermodynamics with an emphasis on how the laws affect the real wold measurements. It will use the basic concepts of the Carnot engine to illustrate how one might go about developing such measurements. The significance, limits, and possibilities will be touched upon as the framework is laid down.

Reversible processes are important. There are four laws of thermodynamics, numbered 0 through 3. These laws hold for all systems. The Carnot engine is the most efficient engine there is. Entropy is an important quantity which is related to heat flow. You can only define entropy well in the thermodynamic limit. A Carnot engine is a good way to do work and to measure temperature.

In thermodynamics we consider a macroscopic system and our variables are global averages. The thermodynamic variables that uniquely determine the thermodynamic state are called state variables. To relate the different variables to each other we use two kinds of relations. The first are the thermodynamic laws, which hold for all systems. The zeroth law discusses the conditions for thermal equilibrium. The first law is a statement about the conservation of energy. The second law is a statement about maximal entropy in equilibrium. The third law is putting the entropy to be zero at zero absolute temperature. The second type of relations are the equations of state, which depend on our specific system. The equations of state can be used only when the system is in equilibrium. For this point it is important to define two types of processes,

reversible and irreversible.

B.2 Summaries for chapter 2.

Energy is stored in a gas. There are many different free energies because there are many different variables involved in a process. Response functions such as heat capacities are the most important way to obtain information. Thermodynamic processes have many variables involved. Hence, the calculus of many variables is used. When two systems come into contact, they are able to exchange energy by exchanging their extensive variables. Fluctuations play a role in materials.

Chapter two introduces the minimum energy principle and discusses the consequences of things changing. The internal energy of a closed system is a minimum as a function of all parameters that are not fixed by external constraints. Internal energy also gives an upper bound for the amount of work that can be done in an irreversible process. One way to see the consequences of changing variables is via free energy. There are many different constructions for free energies, such as the Helmholtz free energy, the Gibbs potential, enthalpy, and the grand potential. Each of these formulations is useful in different situations, depending on the system we are describing and the set of natural variables used with that system. Once you decide which set of variables to use, you can use response functions, such as heat capacities, compressibilities, and the coefficient of thermal expansion to describe the effect of allowing your variables to change. Response functions help us describe the relationships between different thermodynamic variables and tell us a lot about how a system behaves.

The amount of energy which can be released by a gas depends on the process by which the gas is doing work. When trying to measure this energy one needs to decide which variables can, and should be controlled and which ones should be kept constant (eg. Volume may be difficult to measure and Entropy impossible to measure directly, so we may want to keep these variables constant in our measurements). Various "Free Energies" then help us to express the amount of work a system can do with our desired variables held constant. By definition, these Free Energy state functions have exact differentials, and as a result, lead to equivalence relations between various pairs of partial derivatives of many state variables with respect to other state variables (Maxwell Relations). At equilibrium there is minimum energy and maximum entropy with respect to the concerned variables. This fact also leads to conditions on state variables. All intensive variables are the same for an isolated system in thermal equilibrium.

With Newtonian Mechanics we use the Lagrangian and Hamiltonian to get the equations of motion. With the Equations of motion we have a fundamental

understanding of the system that we are working with. In Thermodynamics it is the Energy that we use to get a fundamental understanding of the system. The internal energy is the basic form of energy that we use. If we begin with the internal energy U, we can do successive transforms, or use the Maxwell relations to find properties of the parameters that define the system. Using this method we can arrive at the equation of state for the system, which will define the system. We can also use this to find other measurable parameters, such as the compressibilities and capacitances.

We will start the chapter by introducing the minimum internal energy and maximum entropy principles. Next we will generalize the minimum energy principle to other kinds of thermodynamic potentials (free energies). We will see that the thermodynamic potentials that describe our process depend on the variables under control. For each type of process we define the appropriate thermodynamic potential, among those we will define the Internal Energy (U),Helmholtz (F),Gibbs (G),Entropy (H) and Grand Potential (Ω). Applying a mathematical rules to derive the Maxwell relations which connect changes in different state variables in different processes. Response functions like heat capacity, compressibility, and coefficient of thermal expansion, help us to obtain information about the thermodynamic system. Again we will use mathematical concepts (partial derivatives) to find relations between the response functions and with the help of the minimum energy condition of equilibrium we will derive the inequalities for the heat capacities and compressibilities.Then we will look at the stability requirements on thermodynamic functions other than the internal energy. When it comes to magnetic system we must be careful in our analysis and include the work term comes from the field created in the material. Finally we will briefly discuss a small fluctuation in a thermodynamic limit and derive a very important probability rule.

This chapter begins by introducing the minimum energy principle. This is used to lead into the different free energies and their definitions. Now with the five free energies defined along with the corresponding differential equations, their linear natures (Gibbs-Duhem relations) are explored. These linear relations lead to several important properties such as dependence of some intensive variables on other variables. Maxwell relations are introduced. Next, the basic material properties such as heat capacity or compressibility are defined. A math review of multi-variable calculus is added to the list of tools next. Finally, with these tools, various relationships between material properties and solutions to some problems are examined. During the applications to solutions a perturbational approach involving the role of fluctuations in materials is introduced. A large number of tools are assumed understood, such as the Gaussian nature of Maxwellian functions. After this chapter, there are a large number of problems solvable in thermodynamics with the tools presented. The main body of thermodynamics is presented here.

B.3 Summaries for chapter 3.

Discontinuities in equations of state manifest themselves in the real world as phase transitions. Phase transitions enable us to tell when a material becomes superconductive, or when it's magnetic properties suddenly change, or where general "jumps" occur in values of other extensive state variables. In a simple p-V-T system, the ideal gas law (PV=nRT) doesn't help us to explain phase transitions, so we resort to virial expansions which take interaction between molecules; molecules actually taking up volume etc., into consideration. Van der Waals postulated one such "not-so-ideal gas" equation, valid for both liquid and gas phase. Stability requirements (partial (p) w.r.t. (v) ¡=0) and the minimum energy principle, help us to determine which values of p, V and T are allowable, from our at first seemingly multi-valued Van der Waals equation solution.

Chapter 3 addresses the issue of phase transitions, investigating discontinuities in the equations of state. This is best seen by examining phase diagrams. The lines marked on the p-V diagrams represent the coexistence curves where a system can be in more than one state at a given pressure and temperature. When two such lines meet, we have the triple point, the p and T values at which all 3 phases coexist. For multi-phase diagrams, the maximum number of phases which can coexist is one more than the number of independent intensive state variables needed to describe the system. Crossing a phase boundary leads to a change in state. This change causes a jump in the volume and the other extensive variables, while the energy (but not its derivative) remains continuous. If a system is in a forbidden region of a phase diagram involving an extensive variable, it will phase separate. The Clausius-Clapeyron relation tells us the slope of the coexistence curve in a p-V diagram (which is always positive) and can be expressed in terms of latent heat. The jump in volume of a phase transition is also seen in the van der Waals equation of state in which V is not a unique function of p and T. However, the van der Waals equation allows for states with negative pressures, which are never stable, so this equation is only a good model for a liquid to gas phase transition, ending in a critical point.

In this chapter phase transitions are explored. The boundary is defined. The relationship at the boundary is mathematically modelled in the Clausius-Clapeyron relationship. Latent heats are defined in the context of this relation. Further, the limitations on the possible coexistent phases are informally defined. Some applications are described during the rest of the chapter while introducing additional concepts. Binary systems with chemical reactions are explored. The Van Der Waals equation is next. The Virial expansion is introduced. The rest of the chapter deals with the behavior and validity conditions of the Van Der Waals equation. The asymptotic form is explored to achieve insight.

Phase transitions are discontinuities in the equations of state. In the p versus T diagram, all three phases(solid, liquid, and gas) can coexist at the triple point. Also, the phase boundary between liquid and gas vanishes at the critical point. Two distinct phases can coexist at the phase boundary. We find a phase boundary by looking at the Gibbs free energy for two phases. The number of phases that can coexist depends on the number of independent state variables. The Van der Waals equation of state is a better approximation than the ideal gas law. A line which separates mechanically stable states from mechanically unstable states is a spinodal. A line that separates a thermodynamically meta-stable state with a stable state is a binodal.

In this chapter we will analyze the phase transition phenomena from a macroscopic point of view. Looking at a P-V-T system, we will first analyze the P-T phase diagram and describe the triple point and the critical point. Then we will analyze the V-T diagram which (like P-V diagram) characterized by the forbidden regions. Gibbs free energy analysis yields the Clausius-Clapeyron relation, which gives a quantitative description of the phase boundaries. Next we will generalize our conclusions to a multi phase boundaries and give the binary phase diagrams as an application. Here the point where all three phases can coexist is called eutectic point. To give a more quantitative description of the phase transition we need to know the equation of state. As a first try we will express it in a virial expansion form. The Van Der Waals equation of state is a model which is valid for the change from the gas to the liquid phase. Here we will give a quantitative analysis for such important model.

In chapter 3 we looked at the different ways to represent the phases of materials. We saw that simple materials can have complex even convoluted phase diagrams. Simple binary materials can have highly unstable regions, and there are places in all phases diagrams where materials can simply not exist. We saw that there are co-existence curves for all materials where we can have equal amounts of both phases. There are triple points in all phase diagrams where we can have solid-liquid-gas co-existing at the same time. There are however, no points on any phase diagrams where we can get four phases coming together at the same time. Phase diagrams can be simple or complex, but they give a good description of the system.

B.4   Summaries for chapter 4.

We use order parameters, which are state variables, to distinguish among phases of a system. A useful way to study the free energy per unit volume of a magnetic system is to expand it in terms of the magnetization of the system. Landau studied one such expansion, which only included even powers of the magnetization. This expansion, however, is not valid for when a system is at a phase transition. Ginzberg and Landau modified this expansion to include fluctuations. This

modified form, however, is still incorrect precisely at the phase transition.

What happens at a phase transition? All the techniques and theories discussed so far enable us to model simple equilibrium systems. But what about the fluctuations and discontinuities at and around phase transitions? Chapter 4 presents a good framework to analyze first and second order transitions with the Landau-Ginzburg theory. In order to examine these transitions, we must first determine an order parameter, an extensive state variable that uniquely defines which phase the system is in. To measure the value of the order parameter we need to look at the generalized force associated with it. Landau's method describes phase transitions by parameterizing the free energy as a function of the order parameter. Because of the essential singularity at Tc, Landau's power series fails to converge so it can't explain what happens at the phase transition, but it is good for classifying kinds of phase transitions by comparing the states at both sides of the transition. The order of a phase transition can be defined by its continuity. If it is possible to find a continuous path around a critical point from one phase to another (much like the path around an essential singularity with a branch cut) it is a second order transition. If there is no continuous path, it's a first order transition. In first order transitions, the value of the order parameter is discontinuous at the critical temperature. If we go continuously through a co-existence curve, we end up in a meta-stable state. Near a phase transition, fluctuations become an issue. Ginzburg adapted Landau's theory to better account for the effects of fluctuations by including spatial variations in the order parameter. Ginzburg and Landau further improved the theory with an expansion of the free energy in terms of gradients of the order parameter. This provides a good description of the state of the system much closer to the critical temperature.

We will start this chapter by defining the order parameter and how to measure it. Using a continuity concepts we will define the second order phase transition. Then we will show the similarity between the coexistence curve and the branch cut in a complex function. Giving an overview of a spontaneously broken symmetry before introducing the Landau theory of phase transition. Unlike the van der Waals equation, the Landau theory of phase transition is more general one. Here we will analysis the Landau form of the free energy for the second and first order phase transition, and describe the behavior of the entropy, heat capacity and susceptibility near the critical temperature. Here we will give another definition of the phase transition order, based on the continuity of the order parameter at the critical temperature. Trying to give more accurate description near the phase transition we will study the Ginzburg-Landau theory for fluctuations.

In chapter 4 we began the analysis that will lead us to critical phenomena. We noticed that phase transitions could be modelled by order parameters. Order

parameters are state variables that give the critical phenomena of the system. In the case of chapter 4 we looked at magnetization using Landau-Ginzburg theory, but we know that this model can be used for other spontaneous broken symmetries.

To describe the phase of a system we need a parameter which: 1) differentiates between states of a system, while 2) being measured does not change the system (requires zero field for measurement). Such a state variable is termed an order parameter. When an order parameter and its external field couple to zero, the free energy is usually symmetric as a function of order parameter; so when we have a nonzero order parameter, there are at least 2 states for the system with the same energy. The act of measurement breaks this symmetry. Landau devised a model to parameterize the free energy as a function of order parameter. With an expansion of the free energy w.r.t order parameter we can look at minima and see which values correspond to stable states. At 1st order phase transitions, the Gibbs function is continuous, but derivatives (e.g. (g/T)p =-s and (g/p)T=v) are discontinuous. At 2nd order phase transitions, G and first derivatives are continuous, but second derivatives are discontinuous. We look for phase transitions at discontinuities. . Landau's expansion doesn't converge at the critical points (essential singularities). Fluctuations become important near phase transitions. Fluctuations in a system causes parts of a system to be stable and other parts meta-stable, causing phase separation of the system. Ginzburg, tried to account for fluctuations by making the order parameter a function of position. His model is still not valid at the critical point, but allows us to analyze the system much closer to it.

B.5   Summaries for chapter 5.

Critical exponents show how fast response functions diverge near the critical point. The mean field approach ignores the effects arising from fluctuations in the magnetization. When a system is far away from the critical point, mean field theory is a good approximation. It is not a good approximation, however, close to the critical point. The theory of Ginzberg and Landau gives a better description of a system near the critical point. We use scaling, which has consequences.

What is happening near the critical point and how can we describe the thermodynamic state there? We start by defining the four common critical exponents and discuss the universality behind that. Landau model for superconductivity will be a good example for second order phase transition. Then we discuss the mean field theory, derive the critical exponents for Landau theory, and show that van der waals model is a mean field model. Near the critical point the systems' behavior determined by the fluctuation term of the free energy, which should be homogenous. As a consequence of the scaling we reduce the number

of independent critical exponents. Next we apply the scaling on the pair correlation function and define the hyper scaling. Then we explore the validity of Ginzburg Landau theory. We end the chapter by introducing the time scaling in the correlation function.

Critical exponents help us describe different rates of divergence of response functions, near the critical point. These critical exponents are a unique characterization of phase transitions - i.e. Similar critical exponents indicate similar processes at phase transition. Mean field models produce critical exponents of - b=1/2; a=1; g=0. Van Der Waals used such a model in his equation of state, and these critical exponents were verified. Mean field theory is most useful far away from the critical point. In scaling theory we describe a non-equilibrium state with fluctuations. Including gradient terms in the expansion of free energy, improves our model near the critical point. The pair correlation function describes the average of these fluctuations. Near the critical point only x is important. No matter what you do though, everything still diverges at the critical point and we generally need to throw this whole mean field idea out the window.

Chapter 5 discusses the nature of phase transitions that end in a critical point by focusing on the properties at the critical point (which also determine what happens away from the critical point). In order to characterize the divergent behavior due to fluctuations near the critical point, critical exponents are introduced. They show the speed of the divergence. Critical exponents are a unique characterization of the physics of phase transitions and are used to classify groups of similar transitions with identical exponents. Mean field theory ignores the details of fluctuations by averaging them out. Any mean field theory will always yield the same critical exponents. MFT is a good first approximation for many systems whose measured critical exponents are close to the universal exponents predicted by the theory. Once the critical temperature and pressure are known, the van der Waals equation is unique. We can then use relative variables to write a parameter-free version of this equation to derive values of the critical exponents. If we change the values of the temperature of the field slightly, we see a scaled version of the original picture because the free energy due to fluctuations near a critical point is a homogeneous function of its variables. Near the critical point, the correlation length is the only important length scale, so the energy density exhibits hyper-scaling there. Mean field theory works far away from the critical point. Closer to this point, the model is improved by including gradient terms in the expansions of the free energy. Very close to the critical point, however, we need a different theory.