

Several studies in recent years have demonstrated that upper-division students struggle with partial derivatives and the complicated chain rules ubiquitous in thermodynamics. We asked several experts (primarily faculty who teach thermodynamics) to solve a challenging and novel thermodynamics problem in order to understand how they navigate through this maze. What we found was a tremendous variety in solution strategies and sense-making tools, both within and between individuals. This case study focuses on one particular expert: his solution paths, use of sense-making tools, and comparison of different approaches.

“All of these approaches will get you there eventually, and so... what is the way that... makes it easier for me to organize my thoughts, in terms of finding equations?”

It is perhaps not surprising that students struggle so much with thermodynamics given the complexity of the problem solving skills required even for experts.

ENTER

Find

$$\left(\frac{\partial U}{\partial p}\right)_S$$

using the given equations of state for a van der Waals gas

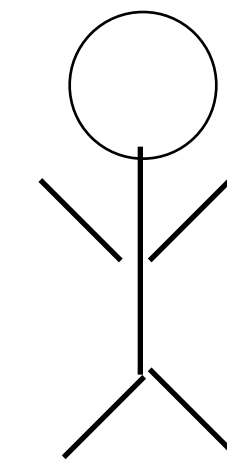
“J” is senior faculty who has taught thermo multiple times

Equations of State

$$U = \frac{3}{2}NkT - \frac{aN^2}{V}$$

$$S = Nk \left\{ \ln \left[\frac{(V - Nb)T^{3/2}}{N\Phi} \right] + \frac{5}{2} \right\}$$

$$p = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$



Dead End #1

Cyclic Chain Rule

Thermodynamic Identity

$$dU = T dS - p dV + \mu dN$$

Response Functions

Partial Derivatives & Differentials

Differentials

Thermodynamic identity & Energy equation of state

Derivatives

Derivatives

Constant S and N

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

$$\left(\frac{\partial U}{\partial p}\right)_S = \frac{3}{2}Nk \left(\frac{\partial T}{\partial p}\right)_S + \frac{aN^2}{V^2} \left(\frac{\partial V}{\partial p}\right)_S$$

Differentials

$$dU = \frac{3}{2}Nk dT + \frac{aN^2}{V^2} dV$$

$$dS = Nk \left(\frac{N\Phi}{V - Nb}\right) (\dots dT + \dots dV)$$

$$dp = \dots dT + \dots dV.$$

Adiabatic Compressibility

Cataloging Tools

Cyclic Chain Rule

$$\left(\frac{\partial A}{\partial B}\right)_C = - \left(\frac{\partial A}{\partial C}\right)_B \left(\frac{\partial C}{\partial B}\right)_A$$

Dividing Differentials

Inversion

$$\left(\frac{\partial A}{\partial B}\right)_C = \left(\frac{\partial B}{\partial A}\right)_C^{-1}$$

1D Chain Rule

$$\left(\frac{\partial A}{\partial B}\right)_C = \left(\frac{\partial A}{\partial D}\right)_C \left(\frac{\partial D}{\partial B}\right)_C$$

2D Chain Rule

$$\left(\frac{\partial A}{\partial B}\right)_C = \left(\frac{\partial A}{\partial B}\right)_D + \left(\frac{\partial A}{\partial D}\right)_B \left(\frac{\partial D}{\partial B}\right)_C$$

Calculating Derivatives

Solve System of Linear Equations

Divide Differentials

Easy from here

Dead End #2

Invert

Cyclic Chain Rule

$$\left(\frac{\partial V}{\partial p}\right)_S$$

1D Chain Rule

1D Chain Rule

Circle: “1=1”

“Nice Sets”

Cyclic Chain Rule

Invert

$$\left(\frac{\partial V}{\partial p}\right)_S = - \left(\frac{\partial S}{\partial V}\right)_T^{-1} \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_S$$

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Dead End #3

Cyclic Chain Rule

Invert

2D Chain Rule

Invert

Derivatives

EXIT

Want constant T, not U

$$\left(\frac{\partial U}{\partial p}\right)_S = -\left(\frac{\partial U}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_U$$

“When I think about these kind of relations... it's like a response function. You simply say, alright, I'm changing one variable, keeping two other variables constant. We have a system here with three independent variables... so, we have a choice here [points to p, S, N] and then measure the change in something else [points to U].”

J stated that the two formalisms (differentials and partial derivatives) were simply “a different encoding of the same information.” Partial derivatives involve ratios of variables and dependent changes (where one has to be sure to choose the right ratios), whereas differentials involve variables and independent changes that connect to create whichever ratio is needed.

Set $dS=0$
& $dN=0$
and
divide
equation
by dp

For J, the relevant differences between using the equation of state and using the thermodynamic identity were that there were now two terms instead of one and that the same tools (various chain rules) would be needed to shift S from an independent variable to a dependent variable.

“I would rather have S as a changing variable, as a dependent variable then as an independent variable.”

“So this is basically, the adiabatic change in volume as a function of pressure, so the adiabatic compressibility here.”

Still no T (save for later)

$$\left(\frac{\partial V}{\partial p}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_p^{-1} \left(\frac{\partial S}{\partial p}\right)_V$$

J looked for what he called “nice sets.” All of the equations of state were in terms of the independent variables $V, T,$ and $N,$ so a nice set would be a partial derivative with respect to one of these, with the other two variables held constant.

$$\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial T}{\partial p}\right)_S$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial p}\right)_S$$

$$\left(\frac{\partial V}{\partial p}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_p^{-1} \left(\frac{\partial S}{\partial p}\right)_V$$

1. set $dS = 0$
 2. solve for dV in terms of dT
 3. substitute dV into dU equation
 4. substitute dV into dp equation
 5. solve for dT in terms of dp
 6. substitute dT into dU equation
- divide dU equation by dp .

“At this point, I have... reduced it to... derivatives which I can take from [the equations of state], cause they... have the right combination of variables.”

Not “nice sets”
Want V, not p

$$\left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_S = \left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial S}{\partial V}\right)_T^{-1}$$