

20 Friday:

Current board:

$\left(\frac{\partial a}{\partial b}\right)_c = \frac{1}{\left(\frac{\partial b}{\partial a}\right)_c}$	$"C_p = \left(\frac{dQ}{dT}\right)_p"$	$dU = TdS - pdV$	
$\left(\frac{\partial a}{\partial b}\right)_d \left(\frac{\partial b}{\partial c}\right)_d = \left(\frac{\partial a}{\partial c}\right)_d$	$\Delta S = \int \frac{dQ_{\text{reversible}}}{T}$	$dF = -SdT - pdV$	$\text{Fairness} = -k \sum_i^{\text{all states}} P_i \ln P_i$
$\left(\frac{\partial a}{\partial b}\right)_c = -\frac{\left(\frac{\partial c}{\partial b}\right)_a}{\left(\frac{\partial c}{\partial a}\right)_b}$	$dU = dQ + dW$	$dH = TdS + Vdp$	$Z \equiv \sum_i^{\text{all states}} e^{-\beta \epsilon_i}$
	$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$	$dG = -SdT + Vdp$	$P_i = \frac{e^{-\beta \epsilon_i}}{Z}$

20.1 Diatomic gas wrapup

Lecture: (20 min) Yesterday we worked out the internal energy per molecule of a diatomic gas associated with translational kinetic energy, rotational kinetic energy, and vibrational energy (which has both a kinetic and potential component). For each case (except translation), you considered both the low- and high- temperature limits.

In each case you had sums that looked like

$$\sum_i \text{something} e^{-\beta E_i} \tag{20.1}$$

and $\beta(E_1 - E_0)$ was either large or small.

For the high-temperature limits, you needed to convert summations into integrals, which was a reasonable approximation because the change of the thing being summed (summand?) was small as you changed the quantum numbers by one, so treating it as a continuum was okay.

For the low-temperature limit, you had an easier scenario, as all the Boltzmann factors were all very small compared with the ground state. So you could just truncate the sum after a few terms.

Translation at high T

$$\frac{U}{N} = \sum_{n_x n_y n_z} \frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2} \frac{1}{Z} e^{-\beta \frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2}} \quad (20.2)$$

$$\approx \int_0^\infty \int_0^\infty \int_0^\infty \frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2} \frac{1}{Z} e^{-\beta \frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2}} dn_x dn_y dn_z \quad (20.3)$$

$$= \frac{\hbar^2 \pi^2}{2mL^2} \frac{1}{Z} \int_0^\infty \int_0^\infty \int_0^\infty (n_x^2 + n_y^2 + n_z^2) e^{-\beta \frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2}} dn_x dn_y dn_z \quad (20.4)$$

$$u_x = \sqrt{\beta} \frac{\hbar \pi}{\sqrt{2mL}} n_x \quad (20.5)$$

$$\frac{U}{N} = \frac{\hbar^2 \pi^2}{2mL^2} \frac{1}{Z} \left(\frac{\sqrt{2mL} \sqrt{k_B T}}{\hbar \pi} \right)^3 \int_0^\infty \int_0^\infty \int_0^\infty (u_x^2 + u_y^2 + u_z^2) e^{-(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z \quad (20.6)$$

$$= \frac{\sqrt{2mL} (k_B T)^{\frac{3}{2}}}{\hbar \pi} \frac{1}{Z} \int_0^\infty \int_0^\infty \int_0^\infty (u_x^2 + u_y^2 + u_z^2) e^{-(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z \quad (20.7)$$

At this point we've extracted the physics from the integral. It's clearly not zero, and it also isn't infinite, so it's just some number that we can work out later. But we still need Z ...

$$Z = \sum_{n_x n_y n_z} e^{-\beta \frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2}} \quad (20.8)$$

$$\approx \int_0^\infty \int_0^\infty \int_0^\infty e^{-\beta \frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2}} dn_x dn_y dn_z \quad (20.9)$$

$$u_x = \sqrt{\frac{\beta}{2m}} \frac{\hbar \pi}{L} n_x \quad (20.10)$$

$$Z = \left(\frac{\sqrt{2mk_B T} L}{\hbar \pi} \right) \int_0^\infty \int_0^\infty \int_0^\infty e^{-(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z \quad (20.11)$$

$$= \left(\frac{\sqrt{2mk_B T} L}{\hbar \pi} \right) \left(\int_0^\infty e^{-u^2} du \right)^3 \quad (20.12)$$

Once again, we've extracted the physics from the integral, leaving a dry, dimensionless husk. In this case, I cleaned that husk up a bit, so it'll be a bit more compact. Putting these together (with a minimum of simplification, we get:

$$\frac{U}{N} = \frac{\frac{\sqrt{2mL} (k_B T)^{\frac{3}{2}}}{\hbar \pi} 3 \left(\int_0^\infty u^2 e^{-u^2} du \right) \left(\int_0^\infty e^{-u^2} du \right)^2}{\left(\frac{\sqrt{2mk_B T} L}{\hbar \pi} \right) \left(\int_0^\infty e^{-u^2} du \right)^3} \quad (20.13)$$

$$= k_B T 3 \left(\int_0^\infty u^2 e^{-u^2} du \right) \left(\int_0^\infty e^{-u^2} du \right) \quad (20.14)$$

$$= \frac{3}{2}k_B T \quad (20.15)$$

Rotation at low T I'll skip over this, as it isn't very exciting (and it's taking a long time to \LaTeX this). I'll just mention that it drops exponentially to zero at low temperature. This is a universal property of systems with a "gap," which is to say, with a finite energy difference between the ground state and the first excited state.

Rotation at high T

$$Z = \sum_{l=0}^{\infty} \sum_{m=-l}^l e^{-\beta \frac{\hbar^2 l(l+1)}{2I}} \quad (20.16)$$

$$= \sum_{l=0}^{\infty} (2l+1) e^{-\beta \frac{\hbar^2 l(l+1)}{2I}} \quad (20.17)$$

$$\approx \int_0^{\infty} (2l+1) e^{-\beta \frac{\hbar^2 l(l+1)}{2I}} dl \quad (20.18)$$

As it turns out, we can relatively easily do this integral. However, the "+1" terms are insignificant, since l is integrated up to infinity, and the large l contribution dominates. So we can:

$$Z \approx \int_0^{\infty} 2l e^{-\beta \frac{\hbar^2 l^2}{2I}} dl \quad (20.19)$$

$$u = \frac{\hbar l}{\sqrt{2Ik_B T}} \quad (20.20)$$

$$Z = \frac{8Ik_B T}{\hbar^2} \int_0^{\infty} u e^{-u^2} u \quad (20.21)$$

$$(20.22)$$

The integral is easy to do, but there's no urgent need to do so: we have already taken the physics out of the integral.

$$\frac{U}{N} \approx \frac{1}{Z} \int_0^{\infty} 2l \frac{\hbar^2 l^2}{2I} e^{-\beta \frac{\hbar^2 l^2}{2I}} dl \quad (20.23)$$

$$= \frac{1}{Z} 2 \frac{\hbar^2}{2I} \left(\frac{4Ik_B T}{\hbar^2} \right)^2 \int_0^{\infty} u^3 e^{-u^2} du \quad (20.24)$$

$$= \frac{2 \frac{\hbar^2}{2I} \left(\frac{4Ik_B T}{\hbar^2} \right)^2 \int_0^{\infty} u^3 e^{-u^2} du}{\frac{8Ik_B T}{\hbar^2} \int_0^{\infty} u e^{-u^2} u} \quad (20.25)$$

$$= 4k_B T \frac{\int_0^{\infty} u^3 e^{-u^2} du}{\int_0^{\infty} u e^{-u^2} u} \quad (20.26)$$

$$= kT \quad (20.27)$$

Here we can see much of the essential physics by recognizing that the energy is proportional to $k_B T$ without performing the integrals. I probably have mistakes somewhere in the above, but the final answer is correct.

Harmonic oscillator at high T For the harmonic oscillator, I'll demonstrate a different approach, since I think showing the same approach for the third time in a row is a bit boring.

$$Z = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega_0} \quad (20.28)$$

$$= e^{-\beta\frac{1}{2}\hbar\omega_0} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega_0} \quad (20.29)$$

$$= e^{-\beta\frac{1}{2}\hbar\omega_0} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega_0})^n \quad (20.30)$$

This is just a harmonic series, so we can solve it using the standard trick, where I'll call the series s :

$$s \equiv \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega_0})^n \quad (20.31)$$

$$e^{-\beta\hbar\omega_0} s = e^{-\beta\hbar\omega_0} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega_0})^n \quad (20.32)$$

$$= \sum_{n=1}^{\infty} (e^{-\beta\hbar\omega_0})^n \quad (20.33)$$

$$= \left(\sum_{n=0}^{\infty} (e^{-\beta\hbar\omega_0})^n \right) - 1 \quad (20.34)$$

$$e^{-\beta\hbar\omega_0} s = s - 1 \quad (20.35)$$

$$1 = (1 - e^{-\beta\hbar\omega_0}) s \quad (20.36)$$

$$s = \frac{1}{1 - e^{-\beta\hbar\omega_0}} \quad (20.37)$$

$$Z = \frac{e^{-\beta\frac{1}{2}\hbar\omega_0}}{1 - e^{-\beta\hbar\omega_0}} \quad (20.38)$$

So that's nice. Of course, we still want to find the energy. To do this, we can employ yet another trick—although it's not so hard to do in the high-temperature limit the same way we solved the previous problem. We can recognize that

$$U = \sum_i P_i E_i \quad (20.39)$$

$$= \sum_i E_i \frac{e^{-\beta E_i}}{Z} \quad (20.40)$$

$$= \frac{1}{Z} \sum_i E_i e^{-\beta E_i} \quad (20.41)$$

$$Z = \sum_i e^{-\beta E_i} \quad (20.42)$$

$$\left(\frac{\partial Z}{\partial \beta} \right)_{E_i} = \sum_i -E_i e^{-\beta E_i} \quad (20.43)$$

$$U = - \frac{\left(\frac{\partial Z}{\partial \beta} \right)_{E_i}}{Z} \quad (20.44)$$

So once we have the partition function, we could just take a derivative to find the internal energy. So for the simple harmonic oscillator, we have:

$$\left(\frac{\partial Z}{\partial \beta} \right)_{E_i} = -\frac{1}{2} \hbar \omega_0 Z - \frac{e^{-\beta \frac{1}{2} \hbar \omega_0}}{(1 - e^{-\beta \hbar \omega_0})^2} e^{-\beta \hbar \omega_0} \hbar \omega_0 \quad (20.45)$$

$$= -\frac{1}{2} \hbar \omega_0 Z - \frac{1}{1 - e^{-\beta \hbar \omega_0}} e^{-\beta \hbar \omega_0} \hbar \omega_0 Z \quad (20.46)$$

$$= -\frac{1}{2} \hbar \omega_0 Z - \frac{\hbar \omega_0}{e^{\beta \hbar \omega_0} - 1} Z \quad (20.47)$$

$$\frac{U}{N} = \frac{1}{2} \hbar \omega_0 + \frac{\hbar \omega_0}{e^{\beta \hbar \omega_0} - 1} \quad (20.48)$$

This gives us an exact solution for the internal energy of a simple harmonic oscillator, but we still haven't found the high-temperature limit. To find that, we have to take $\beta \hbar \omega_0 \ll 1$. In this case, we can just use a simple Taylor's expansion approach:

$$\frac{U}{N} = \frac{1}{2} \hbar \omega_0 + \frac{\hbar \omega_0}{e^{\beta \hbar \omega_0} - 1} \quad (20.49)$$

$$\approx \frac{1}{2} \hbar \omega_0 + \frac{\hbar \omega_0}{1 + \beta \hbar \omega_0 - 1} \quad (20.50)$$

$$= \frac{1}{2} \hbar \omega_0 + \frac{\hbar \omega_0}{\beta \hbar \omega_0} \quad (20.51)$$

$$= \frac{1}{2} \hbar \omega_0 + k_B T \quad (20.52)$$

$$\approx k_B T \quad (20.53)$$

This tells us that like the rotational energy, the vibrational energy approaches $k_B T$ per molecule at high temperatures.

There is a general rule which occurs in the classical limit (which is the high-temperature limit), that any quadratic term in the energy ends up providing $\frac{1}{2} k_B T$ to the internal energy. This is called the *equipartition theorem*. Since there are three translational degrees of freedom (v^2 in each direction), the kinetic energy gives us $\frac{3}{2} k_B T$. There are two ways to rotate a diatomic molecule, which gives us an additional $k_B T$. And finally, the vibration has both kinetic and potential energy, which each provide half of the final $k_B T$.