Thermal Physics

Meeting XV

I Last time

II Connection to Thermodynamics

III Extended example: the Einstein Solid

I • Canonical distribution

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$\bar{y} = \frac{\sum_r \bar{y}_r e^{-\beta E_r}}{Z}$$

with $Z = \sum_r e^{-\beta E_r}$

• We proved

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

and

$$\overline{(\Delta E)^2} = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

and

$$\bar{X} = +\frac{1}{\beta Z}\frac{\partial Z}{\partial x} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}$$

II Notice that much as $\ln \Omega$ played a central role in the microcanonical ensemble $\ln Z$ is playing a central role in the canonical one. We've seen that $Z = Z(\beta, x)$, so

$$d \ln Z = \frac{\partial \ln Z}{\partial \beta} d\beta + \frac{\partial \ln Z}{\partial x} dx$$

and so,

$$d \ln Z = -\bar{E}\, d\beta + \beta\, đW$$

It is nice to write this in terms of $d\bar{E}$,

$$d \ln Z = \beta\, d\bar{E} + \beta\, đW - d(\beta \bar{E})$$

or

$$d(\ln Z + \beta \bar{E}) = \beta(d\bar{E} + đW)$$
$$= \beta\, đQ$$

But we know an exact differential related to heat transfer

$$dS = \frac{đQ}{T}$$

So,

$$S = k(\ln Z + \beta \bar{E})$$

Even more cleanly,

$$\bar{E} - TS = -kT \ln Z$$

or

$$\boxed{F = -kT \ln Z}$$

The "Helmholtz free energy".

It is useful to develop one more property of Z before proceeding to applications.

Consider a composite system

$$A^{(0)} = A + A'$$

with the subsystems only weakly interacting. Label states of A by index r so that their energies are E_r and those of A' by s with E_s'. The total energy is then

$$E_{rs}^{(0)} = E_r + E_s'$$

This is the significance of weak interaction — they exchange energy so that they cause each

each other to evolve but the interaction energy can be neglected in the total energy.

Then $Z^{(0)} = \sum_{r,s} e^{-\beta E_{rs}^{(0)}}$

$$= \sum_{r,s} e^{-\beta(E_r + E_s')}$$

$$= \sum_{r,s} e^{-\beta E_r} e^{-\beta E_s'}$$

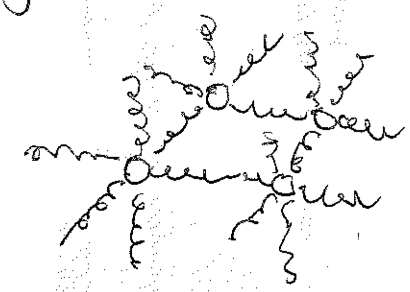
$$= \left(\sum_r e^{-\beta E_r}\right)\left(\sum_s e^{-\beta E_s'}\right)$$

$$\Rightarrow \boxed{Z^{(0)} = Z \cdot Z'}$$

More generally for a total system consisting of N identical composites we have

$$\boxed{Z^{(0)} = Z^N}$$

III Einstein (1907) proposed a very simple model for a solid



and so on...

Assume that all the oscillators are identical. As we discussed the allowed energies of an oscillator are

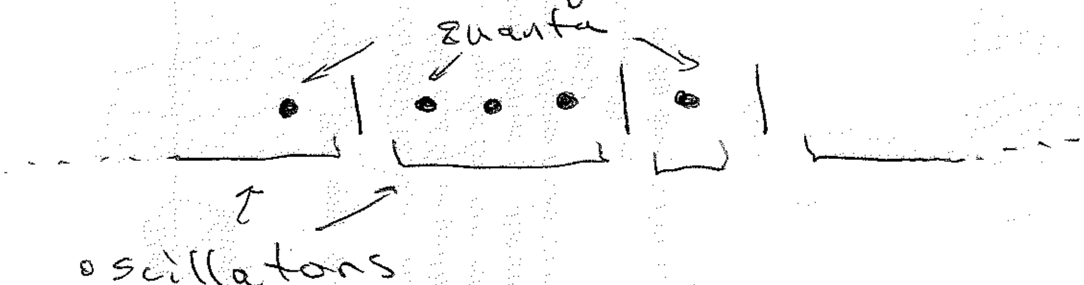
$$E_n = (n+\tfrac{1}{2})\hbar\omega = (n+\tfrac{1}{2})h\nu$$

Notice that every allowed pair of neighboring energies is separated by $\hbar\omega$ or $h\nu$.

Suppose an Einstein solid has q of these quanta of energy shared amongst its N oscillators.

What is $\Omega(N,q)$?

Experiment with small N and q until you get a feel for this. Nice to solve it graphically; e.g. let $N=4$ and $q=5$ then



It is useful to write this as

$$\Omega(N,q) = \frac{N}{N+q}\,\frac{(q+N)!}{N!\,q!}$$

What is S for this system? Keep only the largest terms. Well, $S = k \ln \Omega$ and so

$$\ln\Omega = \ln(q+N)! - \ln N! - \ln q! + \ln\left(\frac{N}{N+q}\right)$$

The total # of symbols is

$$q + N - 1$$

and we want q symbols to be quanta, so we use the choose function

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{(N-1)!\,q!}$$

neglect last term

$$\approx (q+N)\ln(q+N) - N\ln N - q\ln q - (q+N) + N + q$$

$$= (q+N)\ln(q+N) - N\ln N - q\ln q$$

Let's express S in terms of the energy. Recall $E = q\epsilon$ where $\epsilon = \hbar\omega = h\nu$ so,

$$\boxed{\frac{1}{k}S(E) = \left(\frac{E}{\epsilon}+N\right)\ln\left(\frac{E}{\epsilon}+N\right) - N\ln N - \frac{E}{\epsilon}\ln\frac{E}{\epsilon}}$$

Use this entropy to find the temperature of the Einstein solid. Recall,

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

and so,

$$\frac{1}{kT} = \left(\frac{1}{\epsilon}\right)\ln\left(\frac{E}{\epsilon}+N\right) + \left(\frac{E}{\epsilon}+N\right)\cdot\frac{1}{\left(\frac{E}{\epsilon}+N\right)}\cdot\frac{1}{\epsilon}$$

$$-0 - \frac{1}{\epsilon}\ln\frac{E}{\epsilon} - \frac{E}{\epsilon}\cdot\frac{\epsilon}{E}\cdot\frac{1}{\epsilon}$$

or

$$\frac{1}{kT} = \left(\frac{1}{\epsilon}\right)\ln\left(\frac{E}{\epsilon}+N\right) - \frac{1}{\epsilon}\ln\frac{E}{\epsilon}$$

$$+ \frac{1}{\epsilon} - \frac{1}{\epsilon}$$

Then

$$\frac{1}{kT} = \frac{1}{\epsilon}\ln\left(1+\frac{N\epsilon}{E}\right)$$

or

$$\boxed{kT = \frac{\epsilon}{\ln\left(1+\frac{N\epsilon}{E}\right)}}$$

Let's redo this calculation in the canonical framework.

First, calculate the partition function for 1 oscillator.

[Recall that

$$\frac{1}{1-x} = 1+x+x^2+x^3+\cdots$$

For example, it is fun to prove this by long division.]

The energies are $E_r = (r+\frac{1}{2})\hbar\omega$ and it is convenient to drop the zero point energy so that

$$E_r = r\hbar\omega = r\epsilon$$

Then

$$Z_1 = \sum_r e^{-\beta E_r} = \sum_r e^{-\beta\epsilon r}$$

$$= \sum_r \left(e^{-\beta\epsilon}\right)^r$$

$$= \frac{1}{1-e^{-\beta\epsilon}}$$

The total partition function is

$$Z = Z_1^N = \boxed{\left(\frac{1}{1-e^{-\beta\epsilon}}\right)^N}$$

Find the average energy using this partition function.

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left(-N\ln(1-e^{-\beta\epsilon})\right)$$

$$= N\frac{1}{1-e^{-\beta\epsilon}}\cdot(-e^{-\beta\epsilon})(-\epsilon)$$

so that

$$\boxed{\bar{E} = \frac{N\epsilon}{e^{+\beta\epsilon}-1}}$$

Solve this for T and compare with previous result

$$e^{\beta\epsilon}-1 = \frac{N\epsilon}{\bar{E}}$$

$$\Rightarrow \quad \beta\epsilon = \ln\left(1+\frac{N\epsilon}{\bar{E}}\right)$$

This gives

$$\boxed{kT = \frac{\epsilon}{\ln\left(1+\frac{N\epsilon}{\bar{E}}\right)}}$$

just as we found on p5!

It's remarkable how efficient the canonical formalism can be.