Thermal Physics
Meeting XVI

Oct 29th, 2014

I Last time

II A return to interpretation

III Key Properties

IV Monotomic ideal gas

I • Canonical Framework

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} \quad \text{etc.}$$

$$F = -kT \ln Z$$

or

$$S = k \ln Z + \bar{E}/T$$

• N copies of a system

$$Z^{(o)} = Z_1^N$$

• Einstein Solid

$$Z_1 = \sum_r e^{-\beta r \epsilon} = \sum_r \left(e^{-\beta \epsilon}\right)^r$$

$$\Rightarrow \boxed{Z_1 = \frac{1}{1 - e^{-\beta\epsilon}}} \qquad \epsilon = \hbar\omega = h\nu$$

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

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

II So far we have said that the probability of state r is

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

when the system A is at fixed temp. T, i.e. in contact with a heat bath of that temp. Alternatively, we can say that this system has a definite mean energy $\bar{E}$.

You can see this because $\bar{E}$ is completely determined by β and vice versa.

$$\bar{E} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}}.$$

The heat is

$$đQ = d\bar{E} + đW$$

$$= \sum_r E_r dP_r$$

Let's put this all into the entropy

$$S = k\left[\ln Z + \beta \sum_r P_r E_r\right]$$

$$= k\left[\ln Z \cancel{\beta} - \sum_r P_r \ln(ZP_r)\right]$$

A side note relating to information: let's express everything in terms of P_r

$$\bar{E} = \sum_r E_r P_r$$

So,

$$d\bar{E} = \sum_r (E_r dP_r + P_r dE_r)$$

The work done is

$$đW = \sum_r P_r(-dE_r) = -\sum_r P_r dE_r$$

$$= k\left[\ln Z - \ln Z \sum_r P_r - \sum_r P_r \ln P_r\right]$$

$$\Rightarrow \boxed{S = -k \sum_r P_r \ln P_r}$$

Deep connection between ideas in statistical mechanics and ideas in information theory — see work of Shannon.

III We already argued that for two weakly interacting subsystems

$$Z^{(0)} = Z Z' \qquad (1)$$

This means that

$$\ln Z^{(0)} = \ln Z + \ln Z'$$

this leads to the extensivity of $\bar{E}$ and S, e.g.

$$\bar{E}^{(0)} = -\frac{\partial}{\partial \beta} \ln Z^{(0)} = -\frac{\partial \ln Z}{\partial \beta} - \frac{\partial \ln Z'}{\partial \beta} = \bar{E} + \bar{E}' \checkmark$$

and

$$\bar{E}^* = \bar{E} + \epsilon_0,$$

which makes sense. On the other hand

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

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

This also makes sense (the # of states doesn't change when we relabel energies).

A second property is how Z behaves under redefinition of the zero of energy. Let

$$E_r^* = E_r + \epsilon_0$$

Then

$$Z^* = \sum_r e^{-\beta(E_r + \epsilon_0)} = e^{-\beta \epsilon_0} \sum_r e^{-\beta E_r}$$

$$= e^{-\beta \epsilon_0} Z$$

Then

$$\ln Z^* = \ln Z - \beta \epsilon_0$$

<u>Classical limit</u>: suppose we can treat the system classically, so that

$$E = E(q_1, \dots, q_f, p_1, \dots, p_f)$$

then

$$Z = \underbrace{\int \cdots \int}_{2f \text{ integrals}} e^{-\beta E(q_1, \dots, p_f)} \frac{dq_1 \cdots dp_f}{h^f}$$

IV For the ~~gas~~ interacting gas

$$E = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2M} + U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

Let's try it classically,

$$Z' = \int \exp\left\{-\beta\left[\frac{1}{2m}(\vec{p}_1^{\,2} + \cdots + \vec{p}_N^{\,2}) + U(\vec{r}_1, \ldots, \vec{r}_N)\right]\right\} \times \frac{d^3\vec{r}_1 \cdots d^3\vec{r}_N\, d^3\vec{p}_1 \cdots d^3\vec{p}_N}{h^{3N}}$$

or

$$Z' = \frac{1}{h^{3N}} \int e^{-\beta \frac{\vec{p}_1^{\,2}}{2m}} d^3\vec{p}_1 \cdots \int e^{-\beta \frac{\vec{p}_N^{\,2}}{2m}} d^3\vec{p}_N \int e^{-\beta U(\vec{r}_1, \ldots, \vec{r}_N)} d^3\vec{r}_1 \cdots d^3\vec{r}_N$$

The momentum integrals are relatively tame but the position ones are tricky unless $U = 0$ — in that special (ideal) case — $\int d^3\vec{r}_1 = V$

so that

$$\zeta = \frac{V}{h^3}\left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 = V\left(\frac{2\pi m}{\beta h^2}\right)^{3/2}.$$

Then the partition function is

$$\ln Z' = N\left[\ln V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right)\right].$$

The average energy is

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln Z' = \frac{3}{2}N\frac{1}{\beta} = \boxed{\frac{3}{2}NkT}$$

and

$$Z' = \zeta^N$$

where

$$\zeta \equiv \frac{V}{h^3}\int_{-\infty}^{\infty} e^{-\beta \frac{\vec{p}^{\,2}}{2m}} d^3\vec{p}$$

So that

$$\ln Z' = N \ln \zeta$$

Let's do the integrals, which are gaussian

$$\zeta = \frac{V}{h^3}\left(\int_{-\infty}^{\infty} e^{-\beta \frac{p_x^2}{2m}} dp_x\right)^3$$

The average pressure is

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z'}{\partial V} = \frac{N}{\beta}\frac{1}{V} \Rightarrow \boxed{\bar{p}V = NkT}$$

The entropy is

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

$$= \boxed{Nk\left[\ln V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right) + \frac{3}{2}\right]}$$

This is wrong! Not extensive!!