Thermal Physics
Meeting $\underline{XIV}$

I Last time

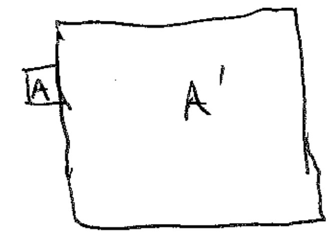
II Examples of Canonical distribution continued

III Computational Power!

IV Connection with thermodynamics

I. • Canonical Distribution

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



• Average Values

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

• Paramagnetism

A spin in a bath of temp. T:

$$\bar{\mu}_H = \mu \tanh \frac{\mu H}{kT}$$

$$= \mu \left(\frac{e^{\frac{\mu H}{kT}} - e^{-\frac{\mu H}{kT}}}{e^{\frac{\mu H}{kT}} + e^{-\frac{\mu H}{kT}}} \right)$$

II $\underline{\text{Ex 1}}$ The magnetization $\bar{M}_0$ is the mean magnetic moment per unit volume

$$\bar{M}_0 = N_0 \bar{\mu}_H$$

where N_0 spins fit in the unit vol,

For large T, really $\frac{\mu H}{kT} \ll 1$,

$$\bar{\mu}_H \simeq \mu \left(\frac{1 + \frac{\mu H}{kT} - \left(1 - \frac{\mu H}{kT}\right)}{2} \right) = \frac{\mu^2 H}{kT}$$

So that,

$$\bar{M}_0 = \frac{N_0 \mu^2}{KT} H$$
$$= \chi \; H$$

where χ is the "magnetic susceptibility". Similarly case check:

$$\bar{M}_0 = N_0 \mu \qquad \frac{\mu H}{KT} \gg 1$$

and so,

$$P(\vec{r},\vec{p})\, d^3\vec{r}\, d^3\vec{p} \propto \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} e^{-\beta(\vec{p}^2/2m)}$$

Doesn't depend on $\vec{r}$! It shouldn't! No position in the gas is special.

On the other hand, some momenta are

$$P(\vec{p})\, d^3\vec{p} = \int_{(\vec{r})} d^3\vec{r}\, d^3p\, P(\vec{r},\vec{p}) \propto e^{-\beta(\vec{p}^2/2m)} d^3\vec{p}$$

<u>Ex 2</u> What is the probability that one of the molecules of an ideal gas is between $\vec{r}$ and $\vec{r}+d\vec{r}$ and has momentum between $\vec{p}$ and $\vec{p}+d\vec{p}$?

Well, $E = \frac{1}{2}m\vec{v}^2 = \frac{\vec{p}^2}{2m}$.

Divide allowed region into cells of size h, then prob. of any one cell is $e^{-(\vec{p}^2/2m)\beta}$

or

$$P'(\vec{v})d^3\vec{v} = C\, e^{-\beta m\vec{v}^2/2}\, d^3\vec{v}$$

"Maxwell distribution"

<u>Ex 3</u> What if the gas is in a cylinder in this room (gravity)?

$$E = \frac{\vec{p}^2}{2m} + mgz$$

$$P(\vec{r},\vec{p})\,d^3\vec{r}\,d^3p \propto \frac{d^3\vec{r}\,d^3\vec{p}}{h}\,e^{-\beta(\vec{p}^2/2m)-\beta mgz}$$
$$= \frac{d^3\vec{r}\,d^3\vec{p}}{h}\,e^{-\beta(\vec{p}^2/2m)}\,e^{-\beta mgz}$$

But then

$$P(\vec{p})\,d^3p = \int_{(r)} P(\vec{r},\vec{p})\,d^3\vec{p}\,d^3\vec{r} = C\,e^{-\beta(\vec{p}^2/2m)}\,d^3\vec{p}$$

It's the same! But

$$P(z)\,dz = \int_{(x,y)}\int_{\vec{p}} P(\vec{r},\vec{p})\,dx\,dy\,d^3\vec{p}$$

or

$$P(z)\,dz = C'\,e^{-\beta mgz}\,dz$$

That is

$$P(z) = P(0)\,e^{-\beta mgz}$$

III From what we've said

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

Let

$$Z \equiv \sum_r e^{-\beta E_r}$$

the "partition function".

Note that

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

So,

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

It gets better – canonical distribution contains systems with a variety of energies, what range?

$$\overline{(\Delta E)^2} = \overline{(E-\bar{E})^2} = \overline{E^2} - \bar{E}^2$$

Let's see

$$\overline{E^2} = \frac{\sum_r E_r^2 e^{-\beta E_r}}{Z}$$

but

$$\frac{\partial^2 Z}{\partial \beta^2} = \sum_r E_r^2 e^{-\beta E_r}$$

$$= \overline{E^2}\, Z$$

so

$$\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$$

Mess around

$$\frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$$

or

$$\overline{E^2} = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) + \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2$$

$$= -\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2$$

Then

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

Of course, it would be nice to have similar results for the work, that is, the equation of state.

Let's recall

$$E_r = E_r(x) \quad \text{external parameter}$$

and

$$đW_r = -dE_r = -\frac{\partial E_r}{\partial x}\,dx$$

We call

$$X_r = -\frac{\partial E_r}{\partial x}$$

a "generalized force" because it may not have units of force but acts like one mathematically.

Consider a quasistatic change dx in an ensemble of similar systems then

$$đW = \bar{X}\,dx = -\overline{\frac{\partial E_r}{\partial x}}\,dx$$

This looks like something we can extract from our canonical ensemble!

$$\frac{\partial Z}{\partial x} = \sum_r (-\beta)\frac{\partial E_r}{\partial x} e^{-\beta E_r}$$

so,
$$\frac{\partial \overline{E_r}}{\partial x} = -\frac{1}{\beta Z}\frac{\partial Z}{\partial x}$$

but then
$$\boxed{đW = \frac{1}{\beta Z}\frac{\partial Z}{\partial x}\,dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}\,dx}$$

Of course, $\boxed{\bar{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}}$

The case we love is $x = V$
$$đW = \bar{p}\,dV = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}\,dV$$

$Z = Z(\beta, x)$, so

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

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

$$= -\bar{E}\,d\beta + \beta\, đW$$

Nice to write this in terms of $d\bar{E}$

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

so,
$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$$

Discussion stopped here. Will pick up rest in meeting XV

IV Notice that much as $\ln \Omega$ played a central role in the microcanonical ensemble $\ln Z$ is playing a similar role in the canonical one. We've just seen that

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

Even more cleanly, $\boxed{F = -kT\ln Z}$.