Thermal Physics

Meeting VII

I. Last time

II. Quantitative characterization of sharpness of P(E)

III Mechanical and thermal equilibrium

IV Math interlude. What is đ?

V Putting it all together! using micro picture to calculate ideal gas.

I

$$\boxed{kT \approx \frac{\bar{E}}{f}}$$

Introduced the extensive vs. intensive distinction

Heat reservoir: $\left|\frac{\partial \beta'}{\partial E'} Q'\right| \ll \beta'$

Led to

$$\Delta S' = \frac{Q'}{T'}$$

and more generally

$$dS = \frac{đQ}{T}$$

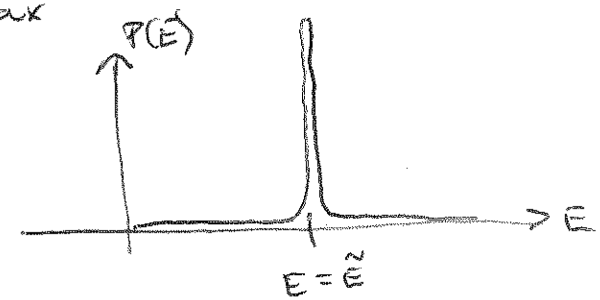
A factor that turns an inexact differential into an exact one is called "an integrating factor".

II Recall

$$P(E) = C\,\Omega(E)\,\Omega'(E')$$

$$\ln P(E) = \ln C + \ln \Omega(E) + \ln \Omega'(E')$$

Call $\tilde{E}$ the energy where P(E) is max



Let $\eta = E - \tilde{E}$ then

$$\ln \Omega(E) = \ln \Omega(\tilde{E}) + \frac{\partial \ln \Omega}{\partial E}\eta + \frac{1}{2}\frac{\partial^2 \ln \Omega}{\partial E^2}\eta^2 + \dots$$

$$= \ln \Omega(\tilde{E}) + \beta\eta - \frac{1}{2}\lambda\eta^2 + \dots$$

where

$$\beta \equiv \frac{\partial \ln \Omega}{\partial E} \qquad \lambda \equiv -\frac{\partial^2 \ln \Omega}{\partial E^2} = -\frac{\partial \beta}{\partial E}.$$

Also, $E' = E^{(0)} - E$, $\Omega'_{max}(\tilde{E}')$,

$$E' - \tilde{E}' = E^{(0)} - E - (E^{(0)} - \tilde{E})$$
$$= -(E - \tilde{E}) = -\eta$$

so

$$\ln \Omega'(E') = \ln \Omega'(\tilde{E}') + \beta'(-\eta) - \tfrac{1}{2}\lambda'(-\eta)^2 + \dots$$

We have argued for gaussians

$$\bar{E} = \cancel{E}\,\mu = \tilde{E}$$
in our case

and

$$\Delta^* E = \sqrt{\sigma^2} = \sqrt{\frac{1}{\lambda_0}} = \lambda_0^{-1/2}$$
in our case

Now suppose $\lambda_0 \sim \lambda$ and $\Omega \propto E^f$

then
$$\beta = \frac{\partial \ln \Omega}{\partial E} = f \cdot \frac{1}{\bar{E}}$$
$$\lambda = -\frac{\partial \beta}{\partial E} = -\frac{-f}{\bar{E}^2} = \frac{f}{\bar{E}^2}$$

This means

$$\ln[\Omega(E)\Omega'(E')] = \ln[\Omega(\tilde{E})\Omega'(\tilde{E}')]$$
$$+ (\beta - \beta')\eta - \tfrac{1}{2}(\lambda + \lambda')\eta^2 + \dots$$

at the max $\beta = \beta'$, let $\lambda_0 \equiv \lambda + \lambda'$ then

$$\ln P(E) = \ln(P(\tilde{E})) - \tfrac{1}{2}\lambda_0 \eta^2$$

or

$$P(E) = P(\tilde{E})\, e^{-\frac{1}{2}\lambda_0 (E - \tilde{E})^2}$$

$$\lambda_0 \geq 0$$

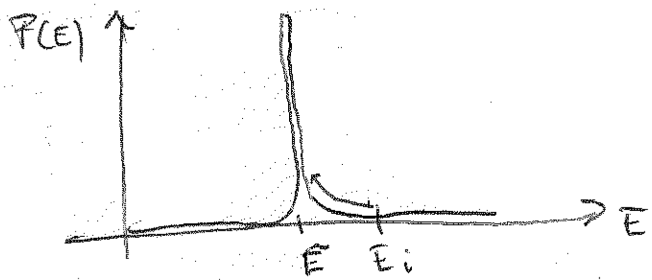
so
$$\Delta^* E = \frac{\bar{E}}{\sqrt{f}}$$

or slightly nicer

$$\boxed{\frac{\Delta^* E}{\bar{E}} = \frac{1}{\sqrt{f}}} \sim 10^{-12} \;!!$$

Very narrow. This is essentially why most experiments measure $\bar{y}$ macro variable no matter what y is.

So our argument that equilibrium occurs when $\Omega^{(0)}$ reaches a max is now quite well supported.
There is generally one maximum that is extremely sharp for systems with macroscopic size.



$$\Rightarrow d\ln\Omega = \beta dE + \beta \bar{p}\, dV$$

Similarly

$$d\ln\Omega' = \beta' dE' + \beta' \bar{p}' dV'$$

$$= -\beta' dE - \beta' \bar{p}' dV \qquad E = E^{(0)} - E' \Rightarrow dE = -dE'$$

So,

$$d\ln\Omega^{(0)} = 0 \Rightarrow$$

$$(\beta - \beta')dE + (\beta\bar{p} - \beta'\bar{p}')dV = 0$$

Let's include one more variable in our scope - say vary volume V.

III Require $\ln\Omega^{(0)}(E, V)$ is max:

$$d\ln\Omega^{(0)} = d(\ln\Omega(E,V) + \ln\Omega'(E',V')) = 0$$

But

$$d\ln\Omega = \frac{\partial \ln\Omega}{\partial E} dE + \frac{\partial \ln\Omega}{\partial V} dV$$

$$= \beta dE + \frac{\partial \ln\Omega}{\partial E}\left(\overline{-\frac{\partial E_r}{\partial V}}\right) dV$$

or $\boxed{\beta = \beta'}$ Thermal and

and $\beta\bar{p} = \beta'\bar{p}' \Rightarrow \boxed{\bar{p} = \bar{p}'}$ mechanical equilib.

How did the pressure really appear in that argument?

$$x \to x + dx \qquad E_r(x) \to \frac{\partial E_r}{\partial x} dx$$

↑ energy each microstate

Introduce

$\Omega_Y(E,x)$ = # states with
Energy $\in [E, E+\delta E]$
external param has value x
and $\partial E_r/\partial x \in [Y, Y+\delta Y]$

Then

$$\Omega(E,x) = \sum_Y \Omega_Y(E,x).$$

$\sigma(E)$ = # states that cross from below E to above E when $x \to x+dx$

By definition

$$\bar{Y} = \overline{\frac{\partial E_r}{\partial x}} = -\bar{X}$$

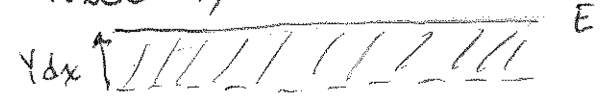
Now,

change in # states when $x \to x+dx$ $= \dfrac{\partial \Omega(E,x)}{\partial x}\,dx$

but also

$$= \sigma(E) - \sigma(E+\delta E) = -\frac{\partial \sigma}{\partial E}\,\delta E$$

For fixed Y,



$$\sigma_Y(E) = \frac{\Omega_Y(E,x)}{\delta E}\,Y\,dx$$

for all Y,

$$\sigma(E) = \sum_Y \frac{\Omega_Y(E,x)}{\delta E}\,Y\,dx$$

$$= \frac{\Omega(E,x)}{\delta E}\cdot\left(\frac{1}{\Omega(E,x)}\sum_Y \Omega_Y(E,x)\,Y\right)dx$$

$$\simeq \frac{\Omega(E,x)}{\delta E}\,\bar{Y}\,dx$$

Then

$$\frac{\partial \Omega}{\partial x}dx = -\frac{\partial}{\partial E}(\Omega\bar{Y})\,dx$$

$$\Rightarrow \frac{\partial \Omega}{\partial x} = -\frac{\partial \Omega}{\partial E}\bar{Y} - \Omega\frac{\partial \bar{Y}}{\partial E}$$

Dividing through by Ω,

$$\frac{\partial \ln\Omega}{\partial x} = -\frac{\partial \ln\Omega}{\partial E}\bar{Y} - \frac{\partial \bar{Y}}{\partial E}$$

Macro system completely dominant

$$\approx -\beta\bar{Y} = \beta\bar{X}$$

We're done it — derived all the thermodynamic laws from micro considerations

0^{th}: $\beta = \beta'$ or $T = T'$ in equilib.

1^{st}: $dE = -đW + đQ$

2^{nd}: $\Delta S \geq 0$ going from one macrostate to another

3^{rd}: $T \to 0_+$ $S \to S_0$ small

because

$$S = k \ln \Omega .$$

~~and~~ Finally,

$$P \propto \Omega \propto e^{S/k} .$$

Basic postulate.

$f = f(x, y, z)$ then by definition

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz$$

redundant notation — $\frac{\partial f}{\partial x}$ means derivative at fixed values of other variables. But, physicists often are lazy about defining $f = f(x, y, z)$ or use the same letter for a different function $f = f(x, y, w)$. So, this notation

IV What is d? Just another kind of derivative. Suppose

Can be clarifying. In physics parlance

df = small change in function f due to change in x, y, or z.

dx = small change in x

In math parlance df is a dual vector, i.e. you feed it a vector to get a number

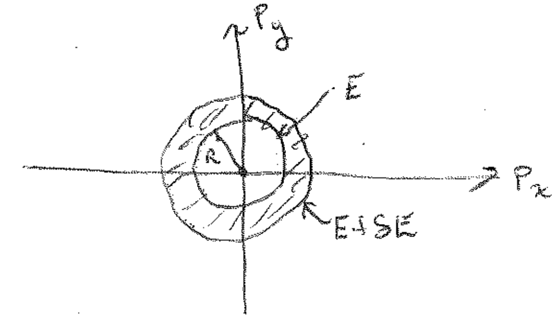
$$df\left(\frac{\partial}{\partial x}\right) = \left(\frac{\partial f}{\partial x}\right)_{y,z} .$$

V For an ideal gas

$$E = K + E_{int} + \cancel{U}^{\to 0}$$

there but neglect it

$$= \sum_{i=1}^{N} \frac{\vec{p}^2}{2M} = \frac{p_{1x}^2}{2M} + \frac{p_{1y}^2}{2M} + \frac{p_{1z}^2}{2M} + \cdots + \frac{p_{Nx}^2}{2M} + \frac{p_{Ny}^2}{2M} + \frac{p_{Nz}^2}{2M}$$



$$R = \sqrt{2mE}$$

$$\Omega(E) \propto \int_E^{E+\delta E} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \, d^3\vec{p}_1 \cdots d^3\vec{p}_N$$

$$= V^N \int_E^{E+\delta E} d^3\vec{p}_1 \cdots d^3\vec{p}_N$$

$$\Phi(E) \propto R^f = (2mE)^{f/2}$$

$$\cancel{\Omega(E) \propto R^{f-1} \propto E^{f/2-1}}$$

$$\Omega(E) = \Phi(E+\delta E) - \Phi(E) = \frac{\partial \Phi}{\partial E}\delta E$$

So $\Omega(E) \propto E^{f/2-1} = E^{\frac{3N}{2}-1}$

Putting this together

$$\Omega(E, V) = B V^N E^{\frac{3N}{2}-1}$$

proportionality constant

Earlier today we derived

$$\boxed{\bar{X} = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial x}}$$

For the ideal gas $x = V$

and $\bar{X} = \bar{p}$ so,

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial V}$$

$$= \frac{1}{\beta}\frac{\partial}{\partial V}\left(\ln B + N \ln V + \ln E^{\frac{3N}{2}-1}\right)$$

$$= \frac{1}{\beta}\frac{N}{V}$$

$$\Rightarrow \quad \bar{p} = kT\frac{N}{V} \quad \text{or} \quad \boxed{\bar{p}V = NkT}!$$