Thermal Physics
Meeting V

I Last time

- Ensemble
- Thermal & Mechanical interaction:

$$d\bar{E} = đQ - đW$$

- Exact and "inexact" differentials. In particular

$$Q = \int_{path} đQ$$

depends on the path or process which transferred the heat.

A strong theme running through all of last week was our basic postulate: All allowed states have equal probability.

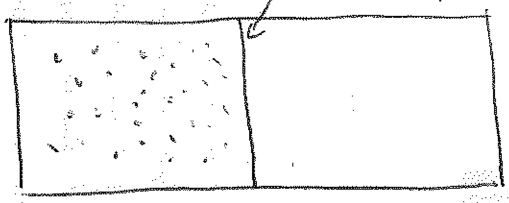
~~We~~ Emphasi~~ze~~s on allowed because ~~more~~ often ~~than not~~ there are some constraints that limit the possible states. Put coords to these macro constraints $y_1, y_2, \cdots, y_n$. The number of allowed States is

$$\Omega = \Omega(y_1, y_2, \cdots, y_n)$$

Removing a constraint increases ~~the~~ this number (or leaves it alone)

$$\Omega_f \geq \Omega_i$$

<u>Wonderful example</u>



Suppose we remove the constraint, the gas evolves into all its allowed states

<u>Prediction 4</u>: ~~Without calculation, intuitively~~ Estimate the order of magnitude of the probability of finding the gas again in this situation

~~a) 10^{-10} b) $10^{-1,000}$~~

a) greater than 10^{-10}

b) between 10^{-10} and $10^{-1,000}$

c) between $10^{-1,000}$ and $10^{-1,000,000}$

d) $10^{-1,000,000}$ and $10^{-1,000,000,000}$

e) less than $10^{-1,000,000,000}$

We know how to calculate this:

~~for each particle~~ the allowed energy

hence momentum stays the same.

For each particle the allowed configuration space doubles

hence

$$P(\tfrac{1}{2}\text{ box}) = \frac{\Omega_i}{\Omega_f}$$

$$= \left(\tfrac{1}{2}\right)^N \leftarrow \text{number of particles}$$

$$= \left(\tfrac{1}{2}\right)^{6\times10^{23}} \approx 10^{-10^{23}}$$

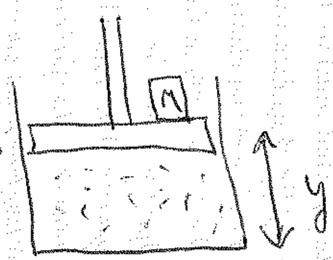
unbelieveably small!

More generally, suppose we unfreeze some one of the constrained variables, call it y, then $P(y)$ = prob. of being between y and $y+dy$ is

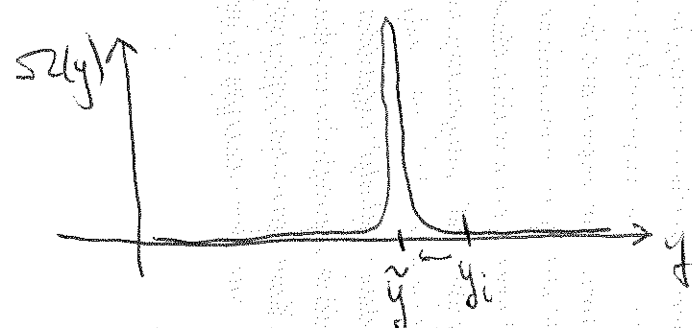
$$P(y) \propto \Omega(y)$$

in equilibrium.

Initially clamped piston

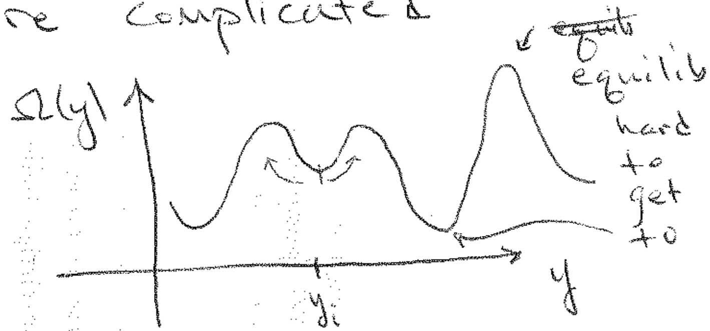


when unclamped will adjust y



If constraints of an isolated system are removed, its parameters tend to adjust so that $\Omega(y_1, \ldots, y_n)$ is a maximum.

Equilibration would be a complicated process if $\Omega(y)$ were complicated



Instead this is generally <u>not</u> the case

How do we know $\Omega(y)$ has this shape? Go back a pick up argument from previous chapter (2).

Fix perspective to our favorite macro observable E.

As always $\Omega(E)$ = # states w/ energy $\in [E, E+\delta E]$

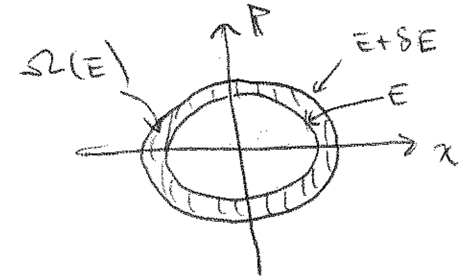
Choose $\delta E >$ quantum level spacing but $\delta E \ll$ macro scale (i.e. E) then

$$\Omega(E) = \omega(E)\,\delta E + O(\delta E^2)$$

$\uparrow$ neglect

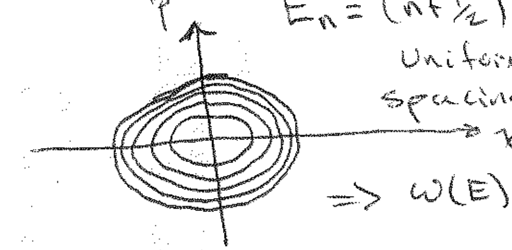
# of states per unit energy range $\equiv$ "density of states"

Think of this as a Taylor expansion.



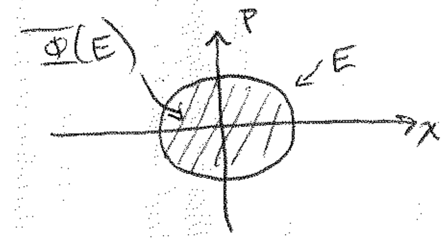
$E_n = (n+\tfrac{1}{2})\hbar\omega$

Uniform spacing in E



$\Rightarrow \omega(E) = \text{const.}$

Also let $\Phi(E) =$ # states in $[0, E]$



<u>Ex</u>: Osc example again

We would like a rough estimate of how $\Omega(E)$ depends on E, when # d.o.f. f is large.

Consider 1 d.o.f. first with energy ϵ. $\Phi_1(\epsilon)$ certainly grows with ϵ,

1 d.o.f.

reasonable that

$$\Phi_1(\epsilon) \propto \epsilon^{\alpha}, \quad \alpha \approx 1$$

The various degrees of freedom roughly share the total energy so

$$\epsilon \approx \frac{E}{f}$$

Each d.o.f has $\Phi_1(\epsilon)$ states and so

$$\Phi(E) \approx \left[\Phi_1(\epsilon)\right]^f \quad \epsilon \approx \frac{E}{f}$$

Use the idea we used on the osc.

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

Then

$$\Omega(E) \approx f\,[\Phi_1(\epsilon)]^{f-1}\frac{\partial \Phi_1}{\partial E}\delta E$$

$$= f\,[\Phi_1(\epsilon)]^{f-1}\frac{\partial \Phi_1}{\partial \epsilon}\frac{\partial \epsilon}{\partial E}\delta E$$

$$= f\,[\Phi_1(\epsilon)]^{f-1}\frac{\partial \Phi_1}{\partial \epsilon}\frac{1}{f}\delta E$$

$$= \Phi_1^{f-1}\frac{\partial \Phi_1}{\partial \epsilon}\delta E$$

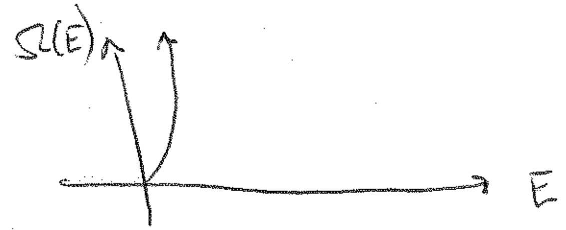
So

$$\ln\Omega \approx f\ln\Phi_1 \approx O(f)$$

for $E > 0$

Excellent. But, you should be complaining "Ha!, I thought you said Ω should be peaked"

So far

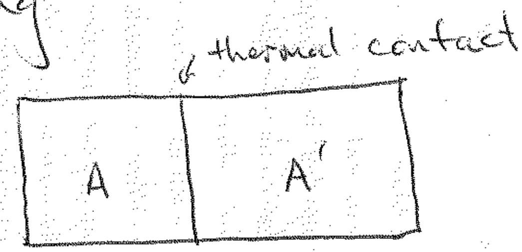


We said Φ_1 increases slowly with ϵ, linearly or even more slowly but $\Phi_1^{f-1} \sim \Phi_1^{10^{23}}$ increases extremely rapidly!

As our prediction 4 illustrates its no fun to deal with $10^{10^{23}}$ so we look at

$$\ln\Omega = (f-1)\ln\Phi_1 + \ln\left(\frac{\partial \Phi_1}{\partial \epsilon}\delta E\right)$$

The "peakedness" comes through interaction,



$$E + E' = E^{(0)} = \text{const.}$$

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

only variable

$\Omega^{(0)}(E) = \#$ states of $A+A'$ when E of $A \in [E, E+\delta E]$

$$P(E) = C\,\Omega^{\circ}(E)$$

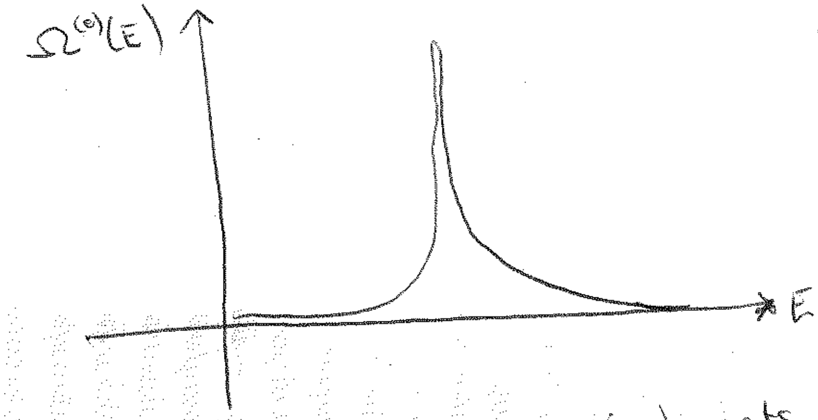
where
$$C = \frac{1}{\sum_E \Omega^{(0)}(E)}$$

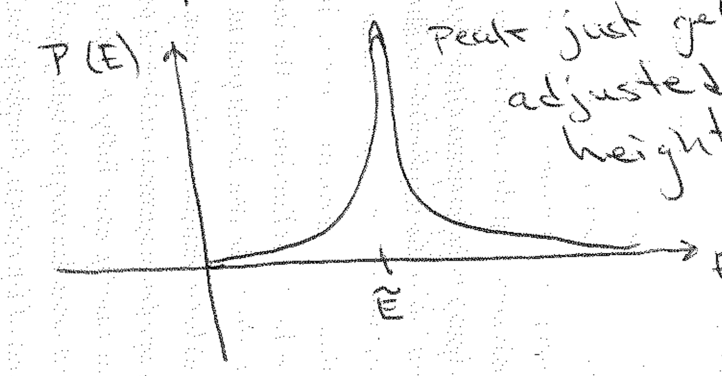
Now,

$$\Omega^{(0)}(E) = \Omega(E)\,\Omega'(\underbrace{E^{(0)} - E}_{\text{as } E \text{ grows } E^{(0)}-E \text{ gets smaller}})$$

and $\Omega(E)$ rapidly increasing, $\Omega'(E^{(0)}-E)$ rapidly decreasing as functions of E

$$P(E) = C\,\Omega(E)\,\Omega'(E^{(0)} - E)$$





Where is $\tilde{E}$? Work with $\ln P$,

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

$$\frac{\partial \ln P}{\partial E} = 0$$

$$\Rightarrow \frac{\partial \ln \Omega(E)}{\partial E} + \frac{\partial \ln \Omega'(E')}{\partial E'}\underbrace{\frac{\partial E'}{\partial E}}_{-1} = 0$$

$$\Rightarrow \beta(\tilde{E}) = \beta'(\tilde{E}')$$

where $\beta \equiv \dfrac{\partial \ln \Omega}{\partial E} = \beta(E)$

Clean up and organize

$$kT \equiv \frac{1}{\beta}$$

T dimensionless $[k]$ = energy

$$S \equiv k \ln \Omega \quad \text{"the entropy"}$$

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

Maximum probability when

$$S + S' = \text{maximum}$$

or

$$T = T'$$

Prediction 5: Bill is 34 years old. He is intelligent but unimaginative compulsive and generally lifeless in school. he was strong in Math but weak in Social studies and humanities.

Rank the likelihood that

a) Bill is a physician who plays poker for a hobby

b) Bill is an architect

c) Bill is an accountant

d) Bill plays Jazz for a hobby

e) Bill surfs for a hobby

f) Bill is a reporter

g) Bill is an accountant who plays Jazz for a hobby

h) Bill climbs Mtns for a hobby.