Thermal Physics
Meetin $\underline{IV}$

I Last time

II Probabilities and Physics

III Interaction

IV Exact and "inexact" differentials

$\underline{I}$

- $H(q,p) = T + V$

  (q_i, p_i) $i = 1, \ldots, N$ Phase Space

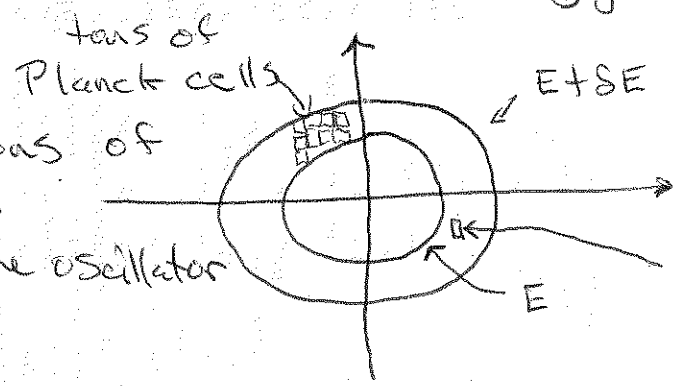
- Quantum Mechanics breaks phase space up into Planck sized cells

- $\underline{\text{Basic postulate}}$: An isolated system in equilibrium is equally likely to be in any of its accesible states

$\underline{\text{Ex.}}$ Our oscillator again ($m=1$)

$$H = \frac{1}{2} p^2 + \frac{1}{2} \omega^2 x^2$$

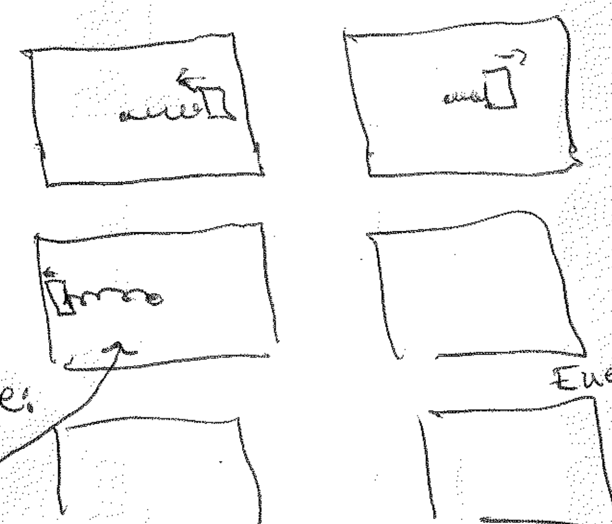
Measured to have energy $\in [E, E+\delta E]$



$\Rightarrow$ tons of states for the oscillator

Basic postulate: all of these equally likely

To talk about this we think of an $\underline{\text{ensemble}}$:



Many instances of the oscillator all with Energy $\in [E, E+\delta E]$ but having different states

(as long as Energy $\in [E, E+\delta E]$)

II Probabilities and Physics

<u>Def</u>: $\Omega(E)$ = total # of states with Energy $\in [E, E+\delta E]$

Similarly let

$\Omega(E; y_k)$ = # of states $[E, E+\delta E]$ and with $y = y_k$

E.g. a given value of pressure.

$$\bar{y} = \frac{\sum_k \Omega(E, y_k)\, y_k}{\Omega(E)}$$

Do Reif 2.4 together.

III Interaction

There are two basic ways that physical systems can interact — this is the key to understanding external parameters (x_i)

Basic postulate $\Rightarrow$

$$P(y_k) = \frac{\Omega(E; y_k)}{\Omega(E)}$$

"All states equally likely, so prob. of finding y_k is just the fraction of states that have $y = y_k$."

And, as before,

Call 'em $x_1, x_2, \cdots x_n$.

The allowed (quantum) ~~energie~~ energies depend on the x_i:

$$E_r = E_r(x_1, x_2, \cdots, x_n)$$

<u>1st type of inter.</u> In the 1st type the external param.'s x_i are held fixed, called "thermal interaction".

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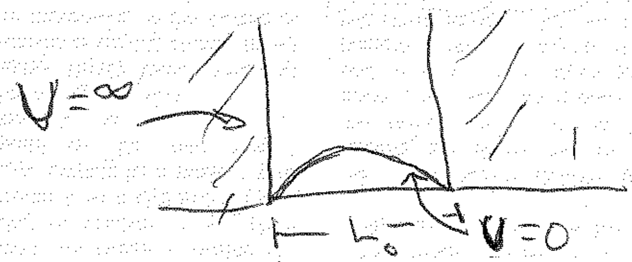
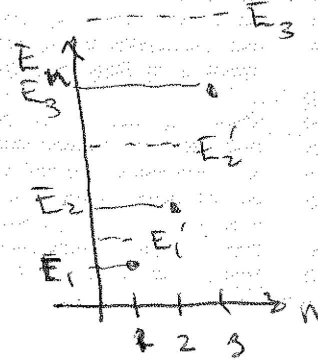
Ex: Particle in Square well



$$E_n = \frac{n^2 \hbar^2 \pi^2}{2 m L_0^2}$$



If we keep L fixed the E_n are fixed!

We can't predict exactly how much energy they exchange — but by drawing many examples from the ensemble we can predict the mean energy exchanged

$Q \equiv \Delta \bar{E}$ "heat absorbed by A"

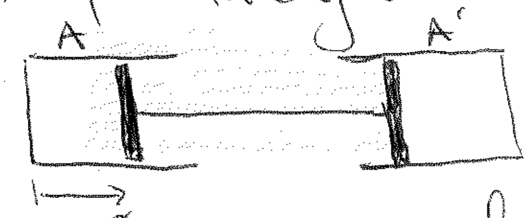
Now, conservation of energy requires

$Q + Q' = 0 \quad (Q' \equiv \Delta \bar{E}')$.

But, we can still give the particle more energy — this excites it to higher energy level. This is what adding heat does. But what is heat?

The ensemble picture helps us understand. Consider A and A' in thermal contact

2nd type of inter.: Thermally insulate (no energy exchange except through changes in x_i).



Again ensemble let's us think about

$\Delta_x \bar{E} \equiv \mathcal{W}$ "work done on A"

More often work with

$W = -\mathcal{W} = -\Delta_x \bar{E}$ "work done by A"

Again cons. of energy gives

$$W + W' = 0$$

Microscopically work changes the allowed energies

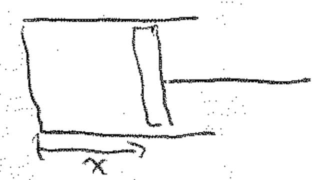
Ex:

$$E_n' = \frac{n^2 \hbar^2 \pi^2}{2m L_f^2}$$

These are larger than E_n's

$$E_n' > E_n \quad \left(\text{for fixed } n\right)$$

It ~~is~~ can be difficult to track how the ensemble is affected by work



A slam on the piston $x \to x_f$ is different from $x \to x_f$ gradually.

But, work is often easily accessed experimentally.

A general interaction combines both of these processes

$$\Delta \bar{E} = \Delta_x \bar{E} + Q = w + Q$$
$$= Q - W$$

Most often we use this in the form

$$d\bar{E} = đQ - đW$$

$đW$ indicates the work done is infinitessimal in the process but not a difference of the "work in the system" because the latter is meaningless.

Let's go into this a little bit

IV Given $F(x,y)$ we have

$$dF = F(x+dx, y+dy) - F(x,y),$$

or

$$dF = \frac{\partial F}{\partial x}\, dx + \frac{\partial F}{\partial y}\, dy$$

$$= A(x,y)\, dx + B(x,y)\, dy.$$

This is an exact differential

So we write

$$\text{đ}G = A'(x,y)\, dx + B'(x,y)\, dy$$

only as a short hand for the R.H.S.

A nice way to capture this is to say that

$$\int_i^f \text{đ}G$$

In particular

$$\Delta F = F_f - F_i = \int_i^f dF$$

But if I randomly choose an $A'(x,y)$ and $B'(x,y)$ then

$$A'(x,y)\, dx + B'(x,y)\, dy$$

might not be s.t.

$$A' = \frac{\partial G}{\partial x} \text{ and } B' = \frac{\partial G}{\partial y}$$

depends on the path taken from i to f while

~~&~~ $\int_i^f dF$

does not. This is a consequence of the fact that

$$\int_i^f dF \overset{\text{always}}{=} F_f - F_i .$$