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Last time: Ideal gas in classical limit - 3D

We wanted to obtain $\Omega(E)$: # of states with energy between E and $E+dE$.

We had $f = 3N$ degrees of freedom.

$$2mE = \sum_{i=1}^{N} \underbrace{\sum_{\alpha=1}^{3} p_{i\alpha}^2}_{|\vec{p}_i|^2} \Rightarrow$$

hypersphere of radius $R(E) = \sqrt{2mE}$ has volume $\propto R^f$

$f = 3N$

$$\Omega(E) \approx \int_{E}^{E+dE} \cdots \int d^3p_1 \ldots d^3p_N \underbrace{\int \cdots \int d^3r_1 \ldots d^3r_N}_{V^N}$$

Lets find $\phi(E)$: # of states with energy smaller than E:

$$\phi(E) \approx V^N \underbrace{(2mE)^{f/2}}_{R^f} \approx V^N E^{\frac{3N}{2}}$$

Last time we saw that

$$\Omega(E) = \frac{\partial \phi(E)}{\partial E} \delta E = V^N \frac{3N}{2} E^{\frac{3N}{2}-1} \delta E \underset{N \gg 1}{\propto} V^N E^{\frac{3N}{2}}$$

Then

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

↳ δE (constant) is included here.

- $\Omega(E)$ increases very rapidly with E if $N \sim 10^{23}$.

Macroscopic systems: (macrostates).

$E_r(x_1, x_2, \ldots, x_n)$: the energy of a microstate r is in general a function of external parameters x_i such as volume, electric field, magnetic field, etc.

Ex: particle in a 3D box of length L:

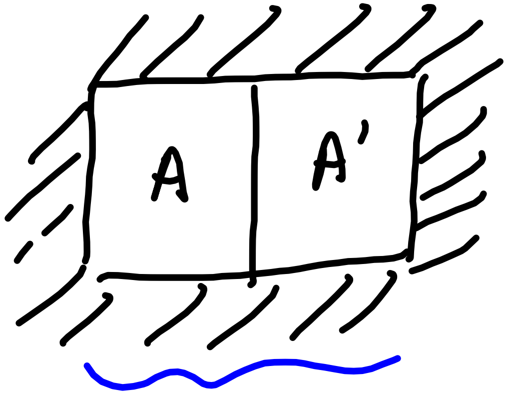
$$E = \frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) \qquad n_i = 1, 2, \ldots$$

E depends on L.

Notice that $(n_x, n_y, n_z) = \left\{ \begin{array}{l} (2,1,1) \\ (1,2,1) \\ (1,1,2) \end{array} \right.$ Same E

∴ 3 microstates correspond to the same macrostate defined by E.

Interactions between macroscopic systems:



A and A' are isolated from the world but can exchange energy.

$A^{(0)}$ is an isolated system. In equilibrium all its accessible states will have equal probability.

Notice that $E^{(0)}$, the energy of $A^{(0)}$ is conserved and $E^{(0)} = \bar{E} + E'$.

1) Thermal interaction :
- only energy is exchanged between A and A'.
- $\{x_i\}$ and $\{x'_i\}$ remain unchanged.

Ex: bottle of beer taken out of the fridge.
After a while it tastes bad.

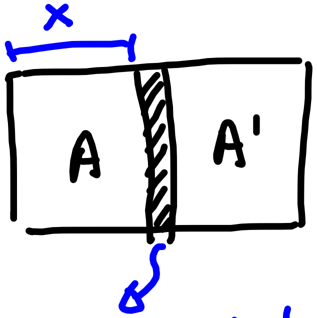
$\Delta \bar{E} \equiv Q$ heat absorbed by A.
mean energy transferred from A' to A.

Since $E^{(0)}$ is constant

$$\Delta \bar{E} + \Delta \bar{E}' = 0 \Rightarrow Q + Q' = 0 \Rightarrow Q' = -Q$$

In this process E_r and E'_r are unchanged but their probability distribution will change.

2) Mechanical interaction:



x can change $\Rightarrow$ x' also will change and then E_r and E'_r will change.

adiabatic: no heat can flow
no energy can be exchanged.

$\tilde{W} = \Delta_x E$ change in energy of system A due to the macroscopic work done on it by system A'.

$W = -\tilde{W} = -\Delta_x \bar{E}$ is the work done by system A.

Notice that $W + W' = 0$ or $W = -W'$

since $E^{(0)} =$ constant.

3) General interaction between A and A':

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

work done by A. (dynamics)

heat absorbed by A. (thermal)

Thermodynamics .

Quasi-static process:

Is a process perform at a rate slow enough so that a system is always in an equilibrium state. In this case

$$dE_r = \sum_{\alpha=1}^{n} \frac{\partial E_r}{\partial x_\alpha} dx_\alpha$$

change in E_r (energy of a microstate) in a quasi-static process in which external parameters x_α are changed.

- We can "follow" E_r.
- The probability of E_r is not changed.

If the change in $\mathcal{E}_r$ is purely mechanical then

$$\delta W_r = -d\mathcal{E}_r = -\sum_{\alpha=1}^{m} \frac{\partial \mathcal{E}_r}{\partial x_\alpha} dx_\alpha =$$

$$= \sum_{\alpha=1}^{m} \underbrace{\frac{-\partial \mathcal{E}_r}{\partial x_\alpha}}_{X_{\alpha,r}} dx_\alpha = \sum_{\alpha=1}^{m} X_{\alpha,r}\, dx_\alpha$$

$X_{\alpha,r}$ and x_α are called conjugate variables.

$X_{\alpha,r}$: generalized force. (Since if dx is a distance then $X_{\alpha,r} = -\frac{\partial \mathcal{E}_r}{\partial r} = \underset{\text{force}}{F}$)

Conjugate pairs:

dx	X	system
L	F	wire
V	p	fluid
M	H	magnet
P	E	dielectric
N	μ	chemical reaction

μ → chemical potential.

For a macroscopic system we can evaluate $\langle X_{\alpha,r} \rangle$ so that

$$\overline{X}_\alpha = -\overline{\frac{\partial E_r}{\partial x_\alpha}}$$

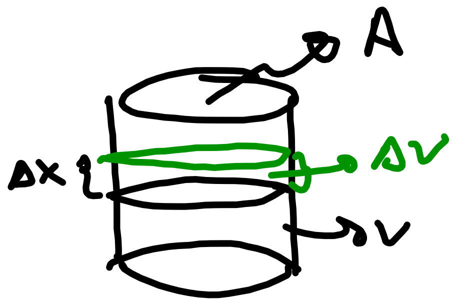
averaged over all the r's in the macrostate.

$$\delta W = \sum_{\alpha=1}^{n} \overline{X}_\alpha \, dx_\alpha$$

macroscopic differential of work.

The macroscopic work W is found by integration over x_α.

If $x_\alpha = V$ and we want to find the work by a gas changing from V to $V + \Delta V$



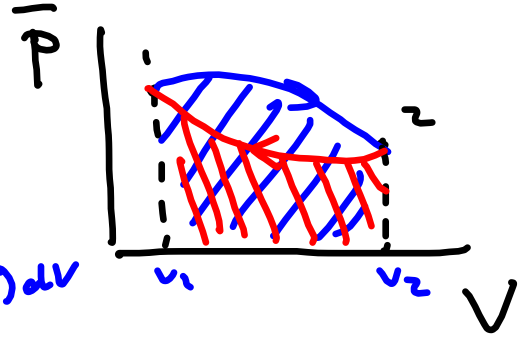
$$dW_r = \bar{F} . \Delta \bar{x} = p_r \underbrace{A \, \Delta x}_{\Delta V} = p_r \Delta V$$

the system will not change microstate in the process.

$$dW_r = -dE_r \quad \therefore \quad p_r = -\frac{\partial E_r}{\partial V}$$

Then at the macroscopic level

$$dW = \bar{p} \, dV$$

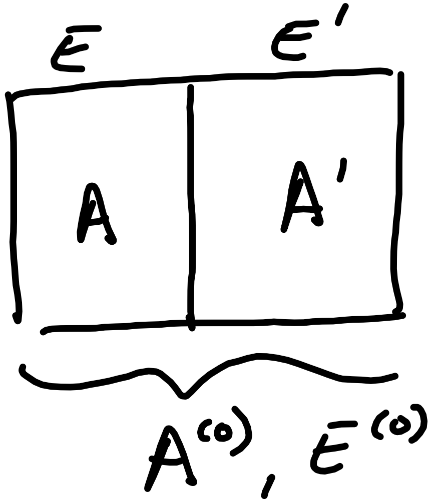


$$W_{1 \to 2} = \int_{v_1}^{v_2} p(v) \, dV$$

$$W_{2 \to 1} = -\int_{v_1}^{v_1} p(v) \, dW$$

Then W depends on the path while ΔE only depends on initial and final state. W is path independent only when $\Delta Q = 0$ (adiabatic process when $dW \equiv dE$).

Thermal interaction between macroscopic systems:



$E^{(0)} = E + E'$ constant

(for A and A' with weak interactions).

$A^{(0)}$ is isolated.

$\Omega(E)$ $\Omega'(E')$ accessible states of A and A'

$$\Omega^{(0)} = \Omega(E)\Omega'(E') = \Omega(E)\,\Omega'(E^{(0)} - E) \quad ①$$

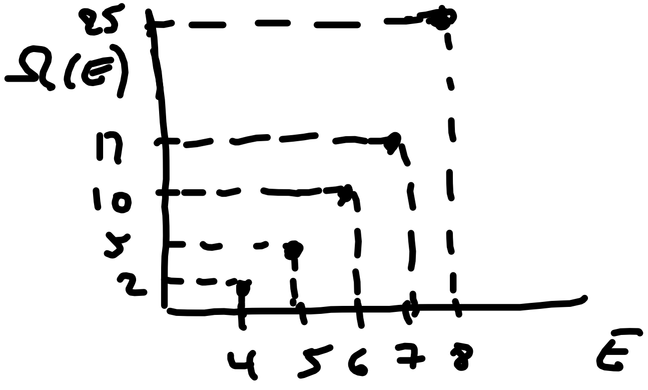
$= \Omega^{(0)}(E)$ it is a function of E despite the fact that $E^{(0)}$ is constant, Let's find the probability $P(E)$ that system $A^{(0)}$ is in one of its accessible states.

$$P(E) = P^{(0)}(E) = C\,\Omega^{(0)}(E) = \frac{\Omega^{(0)}(E)}{\sum_E \Omega^{(0)}(E)}$$

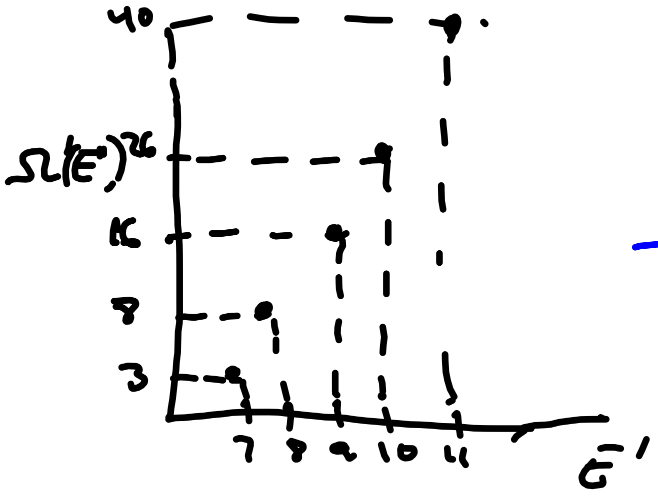
$$C = \frac{1}{\sum_E \Omega^{(0)}(E)}$$

$$P(E) \overset{①}{=} C\,\Omega(E)\,\Omega'(E^{(0)} - E)$$

Example:

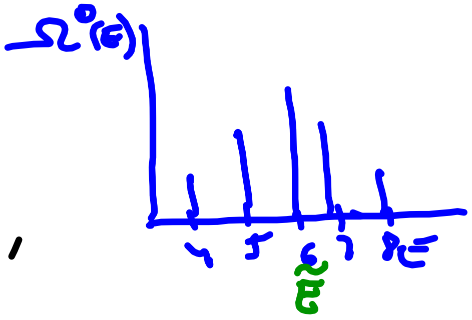


A



A'

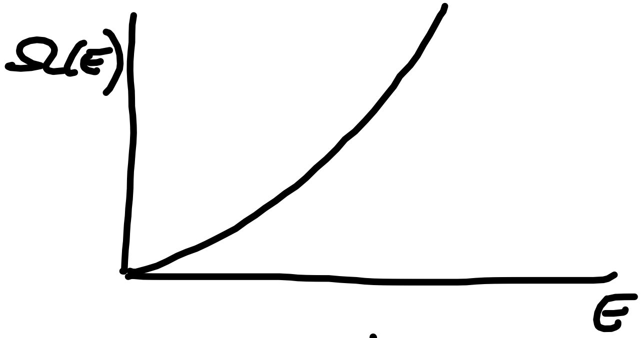
$E^{(0)} = 15$

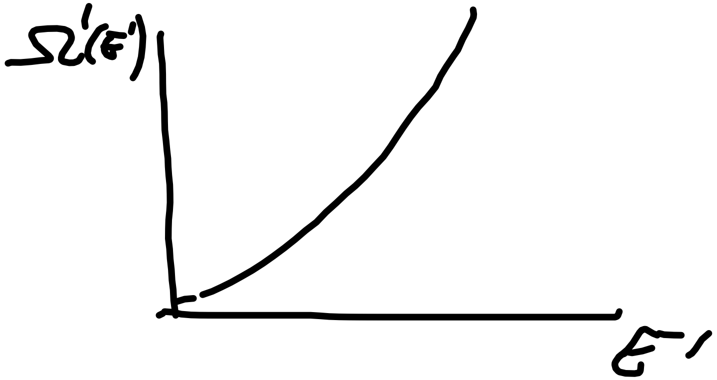


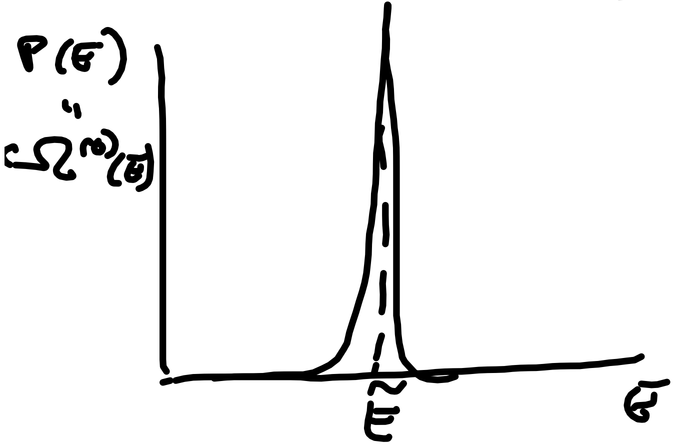
E	E'	$\Omega(E)$	$\Omega'(E')$	$\Omega^{(0)}(E)$	$P(E)$
4	11	2	40	80	.137
5	10	5	26	130	.223
6	9	10	16	160	.275
7	8	17	8	136	.234
8	7	25	3	75	.129

$\tilde{E} = 6$ gives a maximum in $\Omega^{(0)}(E)$

For large numbers (much larger than in the previous example):







P(E) will have a sharp maximum at $E = \tilde{E}$.