IV Microcanonical ensemble

microscopic model → macroscopic laws (thermodynamics)

<u>discrete:</u> states $i = 1, \ldots, \mathcal{N}$ } model
energies E_i

$N(E)$ = # of states with energy E

$S = k_B \ln N(E)$ → thermodynamics

<u>continuous:</u> N particles, phase space $\vec{x} = (\vec{p}_1, \ldots, \vec{p}_N, \vec{q}_1, \ldots, \vec{q}_N)$ } model
energy (Hamiltonian) $H(\vec{x})$

$\Omega(E, V, N) = \int_{H(\vec{x}) \le E} d\vec{x}^N$ phase space volume below energy E

$S = k_B \ln \dfrac{\Omega(E,V,N)}{C_N}$ → thermodynamics

IV 4 The ideal gas

IV 4.1 Classical point of view

$$H(\{\vec{p}_i\}, \{\vec{q}_i\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$$

Want to find $\Omega(E, V, N) = \int_{H(\vec{x}^N) \le E} d\vec{x}^N$

H independent of q

volume of 3N dimensional unit sphere

$$\rightarrow \Omega(E,V,N) = V^N \int_{\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \le E} d\vec{p}^N = V^N \sqrt{2mE}^{\,3N} \, \Omega_{3N}$$

Trick to calculate Ω_{3N}:

$$\int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_{3N} \exp(-x_1^2 - x_2^2 - \cdots - x_{3N}^2) = \sqrt{\pi}^{\,3N}$$

|| polar coordinates

$$\underbrace{\Omega_{3N}\, 3N \int_0^{\infty} r^{3N-1}}_{\frac{d}{dr}\left(r^{3N}\Omega_{3N}\right)} \exp(-r^2)\, dr \overset{x=r^2}{=} \Omega_{3N} \frac{3N}{2} \underbrace{\int_0^{\infty} x^{\frac{3N}{2}-1} e^{-x} dx}_{\Gamma\left(\frac{3N}{2}\right)}$$

$$\Rightarrow \quad \Omega_{3N} = \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)}$$

$$\Gamma(1) = 1 \qquad \Gamma(z+1) = \Gamma(z)z \quad \Rightarrow \quad \Gamma(N+1) = N!$$

$$\Gamma\left(\tfrac{1}{2}\right) = \sqrt{\pi}$$

Back to $\Omega(E,V,N)$:

$$\Omega(E,V,N) = V^N \sqrt{2mE}^{\,3N} \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)}$$

$$\Rightarrow \quad S(E,V,N) = k_B \ln \frac{\Omega(E,V,N)}{C_N}$$

$$= k_B \ln \frac{V^N}{C_N} + \frac{3N}{2} k_B \ln 2\pi m E - k_B \ln \underbrace{\underbrace{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)}_{=\left(\frac{3N}{2}\right)!}}_{\approx \frac{3N}{2}\ln\frac{3N}{2} - \frac{3N}{2}}$$

$$= N k_B \left\{ \frac{3}{2} + \ln\left[\frac{V}{(C_N)^{1/N}} \left(\frac{4\pi m E}{3N}\right)^{3/2}\right]\right\}$$

Consequences:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2} N k_B \frac{1}{E} \Rightarrow E = N \frac{3}{2} k_B T$$

→ ideal gas result, → k_B was the right constant in front of definition of entropy

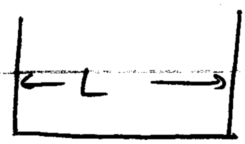
$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = N k_B \frac{1}{V} \Rightarrow pV = N k_B T$$

→ microscopic derivation of ideal gas law
→ entropy definition useful

Remaining question: What is C_N ?
Know: Entropy extensive → $(C_N)^{1/N}$ must be extensive
→ $C_N \sim N^N$

IV.4.2 Quantum-mechanical point of view

"particle in a box"



$H = \frac{p^2}{2m}$
→ discrete energy levels $\epsilon = \frac{h^2}{8mL^2} n^2 \quad n = 1, 2, \ldots$

ideal gas: N particles in three dimensional box $V = L^3$

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m}$$

total energy $E = \frac{h^2}{8mL^2} \sum_{i=1}^{N} (n_{i,x}^2 + n_{i,y}^2 + n_{i,z}^2)$

Similar to continuous system:

for N large

number of states with energy less or equal to E.

$$S = k_B \ln N(E) = k_B \ln \Omega(E)$$

number of states with energy equal to E.

Given E, what is $\Omega(E)$?

$\Omega(E)$ = Number of distinguishable configurations of $\{n_{i,x}, n_{i,y}, n_{i,z}\}$ such that

$$\sum_{i=1}^{N} (n_{i,x}^2 + n_{i,y}^2 + n_{i,z}^2) \leq \frac{8mL^2E}{h^2}$$

= Number of ~~distinguishable~~ lattice points on a $3N$ dimensional lattice within a sphere of radius $\sqrt{\frac{8mL^2E}{h^2}}$

$$= \frac{1}{N!}\left(\frac{8mL^2E}{h^2}\right)^{\frac{3N}{2}} \Omega_{3N} \frac{1}{2^{3N}}$$

since only positive $n_{i,x}, n_{i,y}, n_{i,z}$ occur

since particles are <u>indistinguishable</u>

⇒ All states resulting from a permutation of the particles are actually the same state

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$$S = k_B \ln\left[\left(\frac{2mL^2E}{h^2}\right)^{\frac{3N}{2}} \frac{1}{N!} \Omega_{3N}\right]$$

$$= k_B \ln\left[V^N (2mE)^{\frac{3N}{2}} \Omega_{3N} \frac{1}{h^{3N} N!}\right]$$

Compare to classical calculation

$$\rightarrow \boxed{C_N = h^{3N} N!}$$