MATH327: StatMech and Thermo

Tuesday, 24 February 2026

76 15 03

Something to consider

What should we do with the sum $Z = \sum_i e^{-E_i/T}$ when E_i depends on continuously varying momenta?

Recap

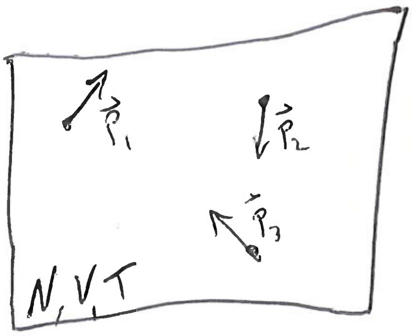
First application of canonical ensemble

Info content → physical effects

Today

Next application: Classical non-rel. ideal gas

$$E_i = \frac{1}{2m} \sum_{n=1}^{N} p_n^2 \quad \text{for micro-state } \omega_i$$



N particles in cubic box

volume $V = L^3$

T fixed by thermal reservoir

Start with partition function $Z = \sum_i e^{-E_i/T}$

problem

micro-states uncountable

depend on continuous $\{\vec{p}_n\}$

Need to regularize system

↓

Countable ω_i with well-defined Z

Then take limit of sums → integrals

Declare only possible momenta are

$$\vec{p} = (p_x, p_y, p_z) = \hbar \frac{\pi}{L}(k_x, k_y, k_z) \quad \text{countable } k_{x,y,z} \in \mathbb{Z}$$

Planck constant

converts units $p \leftrightarrow \frac{1}{L}$

Countable energy levels for each particle

$$\boxed{E_k = \frac{p_k^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} k^2 = \varepsilon(k_x^2 + k_y^2 + k_z^2) \qquad \varepsilon = \frac{\hbar^2 \pi^2}{2mL^2}}$$

$\vec{k} = (2,1,1)$ + perms

Lowest energies $\frac{E}{\varepsilon} = 0, 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, \ldots$

$\vec{k} = (2,2,0)$ + perms

page 57

Not 7, 15, 23, 28, 31, ...

Unlike spin system, not evenly spaced

"Quantized" energies here just ansatz to be removed

For later convenience, restrict $k_{x,y,z} = 0, 1, 2, \ldots$

$\pm k_i \neq 0 \rightarrow$ same k^2, E, $e^{-E/T}$

$\rightarrow$ restriction changes Z by constant factor

no effect on p^2-dependent expectation values

$$\langle f(p^2) \rangle = \sum_i f(p^2)_i \, p_i = \frac{1}{Z} \sum_i f(p^2)_i \, e^{-E_i/T}$$

For single particle

$$Z_1 = \sum_i e^{-E_i/T} = \sum_{k_{x,y,z}=0}^{\infty} \exp\left[-\frac{\varepsilon}{T}(k_x^2 + k_y^2 + k_z^2)\right]$$

$$= \left(\sum_{k_i=0}^{\infty} \exp\left[-\frac{\hbar^2 \pi^2}{2mL^2 T} k_i^2\right]\right)^3$$

Regularized ✓

Take limit of sum → integral

$$Z_1 \to \left(\underbrace{\int_0^\infty}_{\to \frac{1}{2}\int_{-\infty}^{\infty}} \exp\left[\frac{-\hbar^2\pi^2}{2mTL^2} \hat{k}_i^2 \right] d\hat{k}_i \right)^3 \qquad p_i = \frac{\hbar\pi}{L}\hat{k}_i \qquad d\hat{k}_i = \frac{L}{\hbar\pi}\, dp_i$$

continuous

$$Z_1 = \left(\frac{L}{2\pi\hbar} \int_{-\infty}^{\infty} \exp\left[\frac{-p_i^2}{2mT} \right] dp_i \right)^3 = \left(L\sqrt{\frac{mT}{2\pi\hbar^2}} \right)^3 = \left(\frac{L}{\lambda_{th}(T)} \right)^3$$

gaussian $\sqrt{2\pi m T}$

For convenience, define $\lambda_{th}(T) = \sqrt{\frac{2\pi\hbar^2}{mT}} \ll L$

thermal de Broglie wavelength

Generalize to N dist'able particles

$$Z_D = Z_1^N = \left(\frac{L}{\lambda_{th}} \right)^{3N} = \left(\frac{V}{\lambda_{th}^3} \right)^N = \left(\frac{mTL^2}{2\pi\hbar^2} \right)^{3N/2}$$

Depends on volume along with N and T

What about indist'able particles?

Can't be labelled...