MATH327: StatMech and Thermo

Tuesday, 14 April 2026

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Something to consider

We have derived quantum statistics for 'ideal' non-interacting particles.

How good an approximation do you expect this to provide for real physical systems?

Plan

Review big picture, photons

Quantum gases — photon gases

Prob. spaces $\to$ stat. ensembles

Classical statistics: All single-particle micro-states $\to Z_1$

$Z_N \propto Z_1^N$ correct for possible over-counting

Quantum statistics: Sum over all occupation numbers n_ℓ of discrete energy levels E_ℓ

No over-counting!

Photons

Bosons with $E = \hbar\omega = pc$ $\quad p = \hbar\frac{\pi}{L}k$

$n_\ell = 0, 1, 2, \dots$ $\quad \omega\lambda = 2\pi c$ $\quad \sqrt{k_x^2 + k_y^2 + k_z^2}$

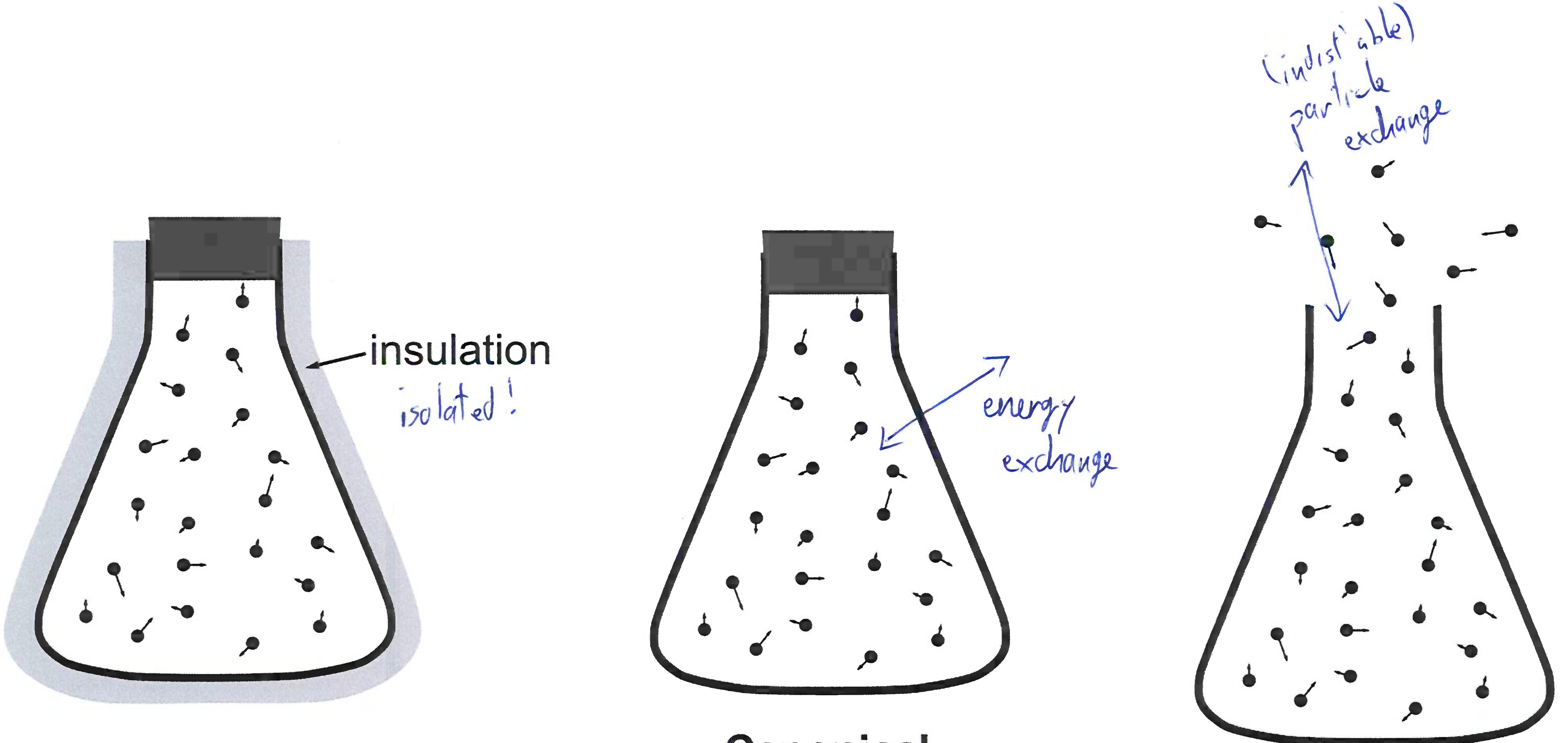
$k_{x,y,z} = 1, 2, 3, \dots$

Photon gas grand-canonical potential

$$\Phi_{ph} = T \sum_\ell \log\left(1 - e^{-\beta(E_\ell - \mu)}\right) = 2T \sum_{\vec{k}} \log\left(1 - e^{-\beta(\hbar\omega - \mu)}\right)$$

$E_\ell > \mu$ $\quad$ polarizations

commons.wikimedia.org/wiki/File:Statistical_Ensembles.png



Microcanonical
(const. N E)

Canonical
(const. N T)

infd. content
ideal gases
therm. cycles

Grand Canonical
(const. μ T)

quantum gases

Simplification: $\mu = 0 < E_\ell$

Photons easy to create and absorb with constant entropy

very little energy $\mu = -T \left.\frac{\partial E}{\partial N}\right|_S = 0$

Simplification: $L \gg \lambda \to$ integrate over closely spaced energy

$$\Phi_{ph} \approx 2T \int \log\left(1 - e^{-\beta\hbar\omega}\right) d^3\hat{k}$$

$$\omega = \frac{pc}{\hbar} = \frac{c\pi}{L}\sqrt{k_x^2 + k_y^2 + k_z^2} \to \text{spherical coords.}$$

$k_{x,y,z} \geq 1$

$\to$ single octant

$$\int d^3\hat{k} = \int_0^\infty \hat{k}^2 \, d\hat{k} \underbrace{\int_0^{\pi/2} \sin\theta \, d\theta}_{1} \underbrace{\int_0^{\pi/2} d\phi}_{\pi/2}$$

$$\Phi_{ph} \approx \pi T \int_0^\infty \hat{k}^2 \log\left(1 - e^{-\beta\hbar\omega}\right) d\hat{k} \qquad \hat{k} = \omega\left(\frac{L}{c\pi}\right)$$

$$= \frac{VT}{c^3\pi^2} \int_0^\infty \omega^2 \log\left(1 - e^{-\beta\hbar\omega}\right) d\omega$$

$$\langle E \rangle_{ph} = -T^2 \frac{\partial}{\partial T}\left(\frac{\Phi_{ph}}{T}\right) + \underbrace{\mu}_{0} \langle N \rangle_{ph} = \frac{\partial}{\partial \beta}\left(\beta \Phi_{ph}\right)$$

Density

$$\boxed{\begin{aligned} \frac{\langle E \rangle_{ph}}{V} &= \frac{1}{c^3\pi^2} \int_0^\infty \omega^2 \frac{\partial}{\partial\beta} \log\left(1 - e^{-\beta\hbar\omega}\right) d\omega \\ &= \frac{1}{c^3\pi^2} \int_0^\infty \frac{\omega^2\left(-e^{-\beta\hbar\omega}\right)\left(-\hbar\omega\right)}{1 - e^{-\beta\hbar\omega}} d\omega \\ &= \frac{\hbar}{c^3\pi^2} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega = \int_0^\infty \underbrace{P(\omega)}_{\text{spectral density}} d\omega \end{aligned}}$$

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$$P(\omega) = \left(\frac{\hbar}{c^3\pi^2}\right) \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$ is Planck spectrum

Change variables to $\lambda = \frac{2\pi c}{\omega}$

$$\omega = \frac{2\pi c}{\lambda}$$

$$d\omega = -\frac{2\pi c}{\lambda^2}\, d\lambda$$

$$\frac{\langle E\rangle_{ph}}{V} = \frac{\hbar}{c^3\pi^2}\int_{\infty}^{0} \frac{(2\pi c/\lambda)^3}{e^{2\pi\beta\hbar c/\lambda}-1}\left(-\frac{2\pi c}{\lambda^2}\right) d\lambda$$

$$= 16\pi^2\hbar c\int_0^\infty \frac{1}{e^{2\pi\beta\hbar c/\lambda}-1}\,\frac{d\lambda}{\lambda^5} = \int_0^\infty P(\lambda)\, d\lambda$$

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$$P(\lambda) = \left(\frac{16\pi^2\hbar c}{\lambda^5}\right)\frac{1}{e^{2\pi\beta\hbar c/\lambda}-1}$$