MATH327: StatMech and Thermo

Thursday, 19 March 2026

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Something to consider

Quantum statistics should reproduce classical results when $\langle n_\ell \rangle \ll 1$

(so multiple particles are unlikely to occupy the same energy level).

What temperatures and chemical potentials correspond to this?

Recap

Classical Maxwell-Boltzmann $Z_g = \prod_\ell \exp\left[e^{-\beta(E_\ell - \mu)}\right]$

Quantum statistics defines micro-states by occupation numbers n_ℓ of energy level E_ℓ

Boson and Fermions

Today

Bose-Einstein and Fermi-Dirac statistics

Classical limit

Photons (prep. for photon gas)

Grand-canonical part. func. for bosons

Sum $n_\ell = 0, 1, 2, \ldots$ for every energy level E_ℓ

Warm-up: Single E_0 with energy E_0

$\boxed{\text{Micro-state energy } E_i = N_i E_0 = n_0 E_0}$

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$$Z_g = \sum_{n_0=0}^{\infty} \exp(-\beta(E_0 n_0 - \mu n_0)) = \sum_{n_0} \left[e^{-\beta(E_0-\mu)} \right]^{n_0}$$

$$= \frac{1}{1-e^{-\beta(E_0-\mu)}}$$

Geometric series only converges for $e^{-\beta(E_0-\mu)} < 1$

$$\beta > 0 \rightarrow E_0 - \mu > 0 \rightarrow E_0 > \mu \quad \checkmark$$

$E_0 \geq 0$ $\qquad \mu = -T \frac{\partial S}{\partial N}\Big|_E < 0$

Generalize to ε_ℓ with $\ell = 0, 1, 2, \ldots \mathcal{L}$

$\{n_\ell\}$ defines micro-states

$$Z_g = \sum_{n_0} \sum_{n_1} \cdots \sum_{n_{\mathcal{L}}} \exp\left[-\beta \sum_\ell (E_\ell - \mu) n_\ell\right]$$

$$= \left(\sum_{n_0} e^{-\beta(E_0-\mu)n_0}\right)\left(\sum_{n_1} e^{-\beta(E_1-\mu)n_1}\right) \cdots \left(\sum_{n_{\mathcal{L}}} e^{-\beta(E_{\mathcal{L}}-\mu)n_{\mathcal{L}}}\right)$$

$$= \prod_\ell \frac{1}{1-e^{-\beta(E_\ell-\mu)}} \qquad E_\ell > \mu$$

Bose-Einstein g.c. part. func.

For fermions, only difference is $n_\ell \in \{0, 1\}$

Single $\varepsilon_0 \rightarrow Z_g = \sum_{n_0=0}^{1} e^{-\beta(E_0-\mu)n_0} = 1 + e^{-\beta(E_0-\mu)}$

General $\varepsilon_\ell \rightarrow Z_g = \prod_\ell \left(1 + e^{-\beta(E_\ell-\mu)}\right)$

Fermi-Dirac g.c. part. func.

Collect results for $\Phi = -T \log Z_g$

$$\Phi_{MB} = -T \log\left[\prod_\ell \exp\left(e^{-\beta(E_\ell-\mu)}\right)\right] = -T\sum_\ell e^{-\beta(E_\ell-\mu)}$$

$$\Phi_{BE} = +T\sum_\ell \log\left(1-e^{-\beta(E_\ell-\mu)}\right)$$

$$\Phi_{FD} = -T\sum_\ell \log\left(1+e^{-\beta(E_\ell-\mu)}\right)$$

Classical MB should emerge from quantum when $\langle N\rangle \ll$ number of accessible energy levels

$p_i \sim e^{-\beta E_i} \rightarrow$ more accessible E_ℓ for small β = high T

Compute $\langle N\rangle = \frac{-\partial}{\partial\mu}\Phi$ for all three and check high T

$$\boxed{\begin{aligned}
\langle N\rangle_{MB} &= T\sum_\ell \frac{\partial}{\partial\mu} e^{-\beta(E_\ell-\mu)} = \sum_\ell \frac{1}{e^{\beta(E_\ell-\mu)}} = \sum_\ell \langle n_\ell\rangle_{MB}\\
\langle N\rangle_{BE} &= -\cancel{T}\sum_\ell \frac{\cancel{+}e^{-\beta(E_\ell-\mu)}\cancel{\beta}}{1-e^{-\beta(E_\ell-\mu)}} = \sum_\ell \frac{1}{e^{\beta(E_\ell-\mu)}-1} = \sum_\ell \langle n_\ell\rangle_{BE}\\
\langle N\rangle_{FD} &= \cancel{T}\sum_\ell \frac{e^{-\beta(E_\ell-\mu)}\cancel{\beta}}{1+e^{-\beta(E_\ell-\mu)}} = \sum_\ell \frac{1}{e^{\beta(E_\ell-\mu)}+1} = \sum_\ell \langle n_\ell\rangle_{FD}
\end{aligned}}$$

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All occupation numbers ≥ 0 ✓

$$\langle n_\ell\rangle_{MB} = \frac{1}{e^{\beta(E_\ell-\mu)}}$$

$$\langle n_\ell\rangle_{BE} = \frac{1}{e^{\beta(E_\ell-\mu)}-1} \qquad \langle n_\ell\rangle_{FD} = \frac{1}{e^{\beta(E_\ell-\mu)}+1}$$

All agree when $e^{\beta(E_\ell-\mu)} \gg 1 \rightarrow \langle n_\ell\rangle \ll 1$ ✓

looks like large β = low T ???

Naive high-T limit $\beta \to 0$ with fixed $(E_\ell - \mu)$ gives

$\langle n_\ell \rangle_{MB} \to 1$ vs. $\langle n_\ell \rangle_{FD} \to \frac{1}{2}$ vs. $\langle n_\ell \rangle_{BE} \to \infty$

Quantum effects important!

Reason: $\langle N \rangle$ also grows

True classical limit needs **both**

$T \to \infty$ (more accessible energy levels)

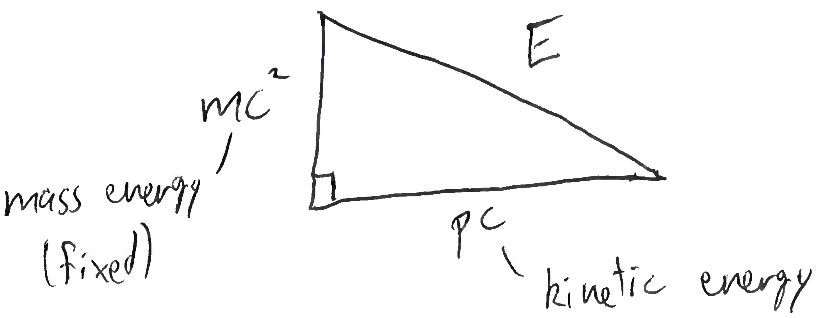
$-\mu \to \infty$ (keep $\langle N \rangle$ from growing)

with $-\mu \gg T \gg E_\ell$ so $e^{\beta(E_\ell - \mu)} \gg 1$ ✓

Applications of quantum stats. in g.c. ensemble

need to specify energy levels $\mathcal{E}_\ell$ and energies E_ℓ

In general $E^2 = (mc^2)^2 + (pc)^2$ $\qquad p^2 = p_x^2 + p_y^2 + p_z^2$



"Einstein's triangle"

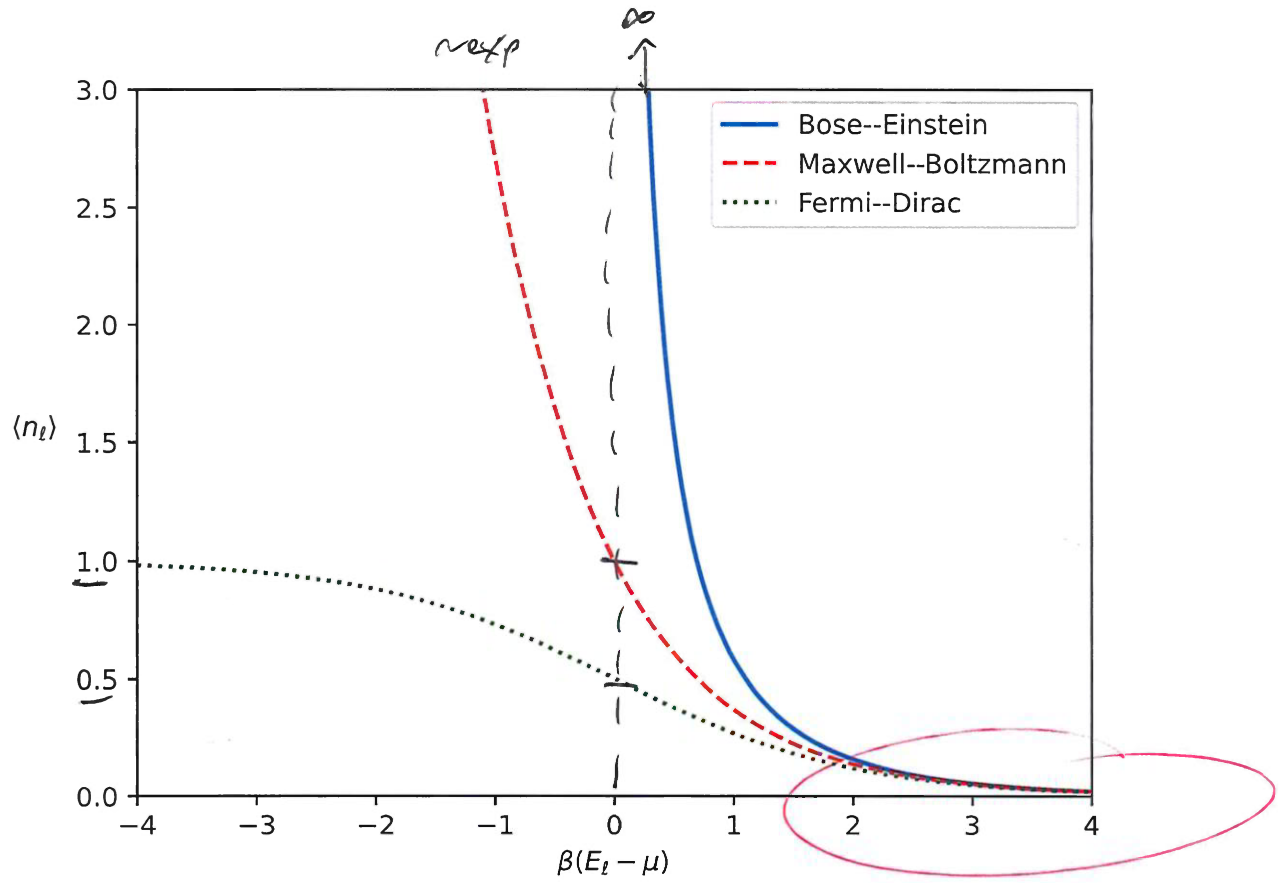
We will consider two simpler limits

1) Ultra-relativistic $\quad p \gg mc \quad$ (including $m=0$)

$E \simeq pc$

2) Non-relativistic $\quad p \ll mc$

$$\boxed{E = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} = mc^2 + \frac{p^2}{2m} + \mathcal{O}\left(\left[\frac{pc}{mc^2}\right]^4\right)}$$



$\sim \exp$
∞
3.0
2.5
2.0
1.5
1.0
0.5
0.0
$\langle n_\ell \rangle$
−4
−3
−2
−1
0
1
2
3
4
$\beta(E_\ell - \mu)$
Bose--Einstein
Maxwell--Boltzmann
Fermi--Dirac

Photons are bosons with $m=0 \rightarrow E_{ph} = pc$

Quanta of electromagnetic ~~field~~ waves (light)

Constant speed of light $c = \frac{\lambda w}{2\pi}$

relates wavelength λ

and angular frequency $w = 2\pi F$

Volume $V = L^3$ quantize frequencies and energies

$$L = k_i \left(\frac{\lambda}{2}\right) \rightarrow \lambda = \frac{2L}{k_i}$$ "wavenumber" $k_{x,y,z} = 1, 2, \ldots$

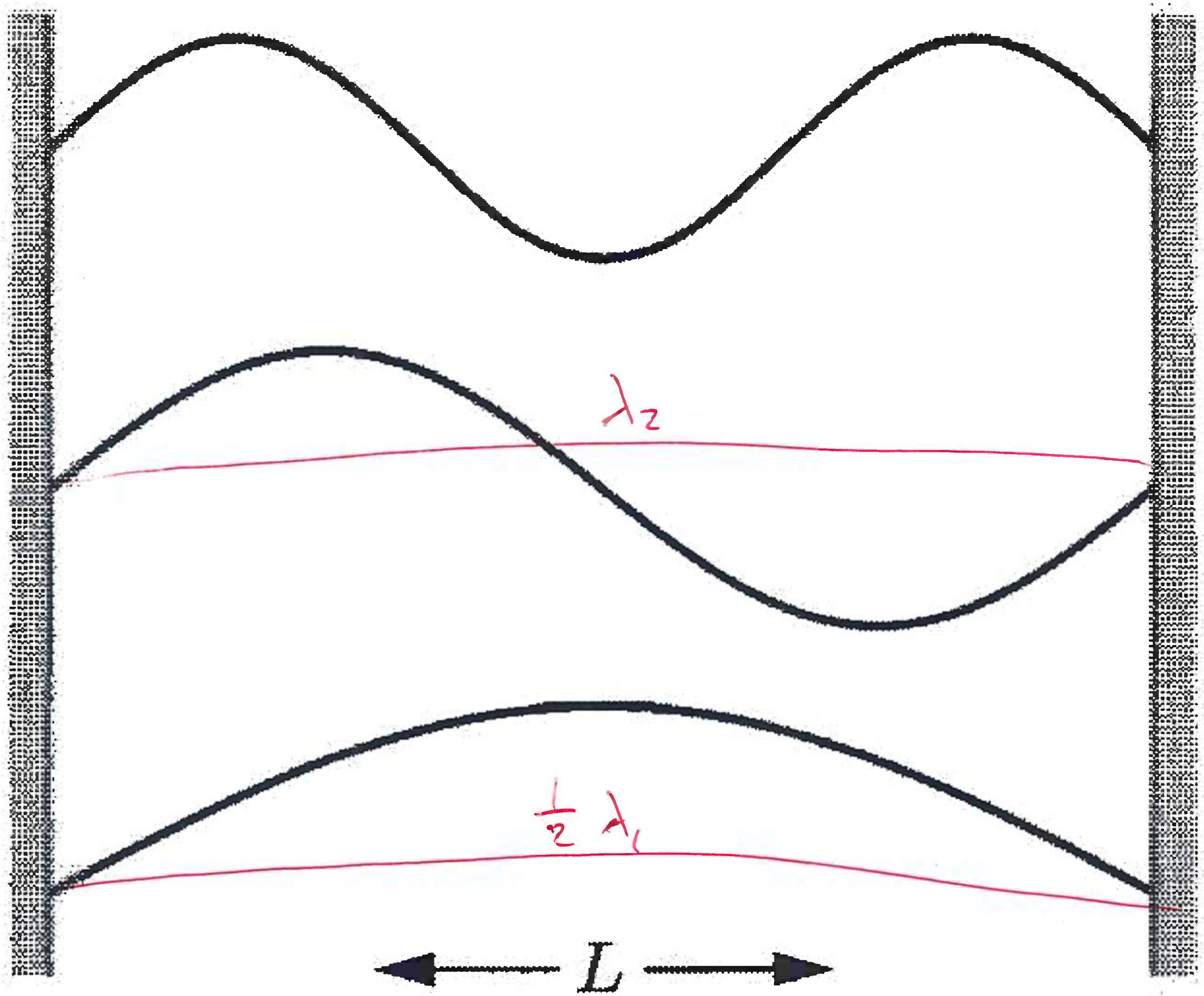
$$w = \frac{2\pi c}{\lambda} = c \frac{\pi}{L} \underbrace{k}_{\sqrt{k_x^2 + k_y^2 + k_z^2}} = c\left(\frac{p}{\hbar}\right)$$ $$p = \hbar \frac{\pi}{L} k$$

$$\therefore E_{ph} = pc = \hbar w$$

Large E ~ high freq. ~ short $\lambda = \frac{2\pi c}{w}$ "ultraviolet"

Small E ~ low freq. ~ large λ "infrared"

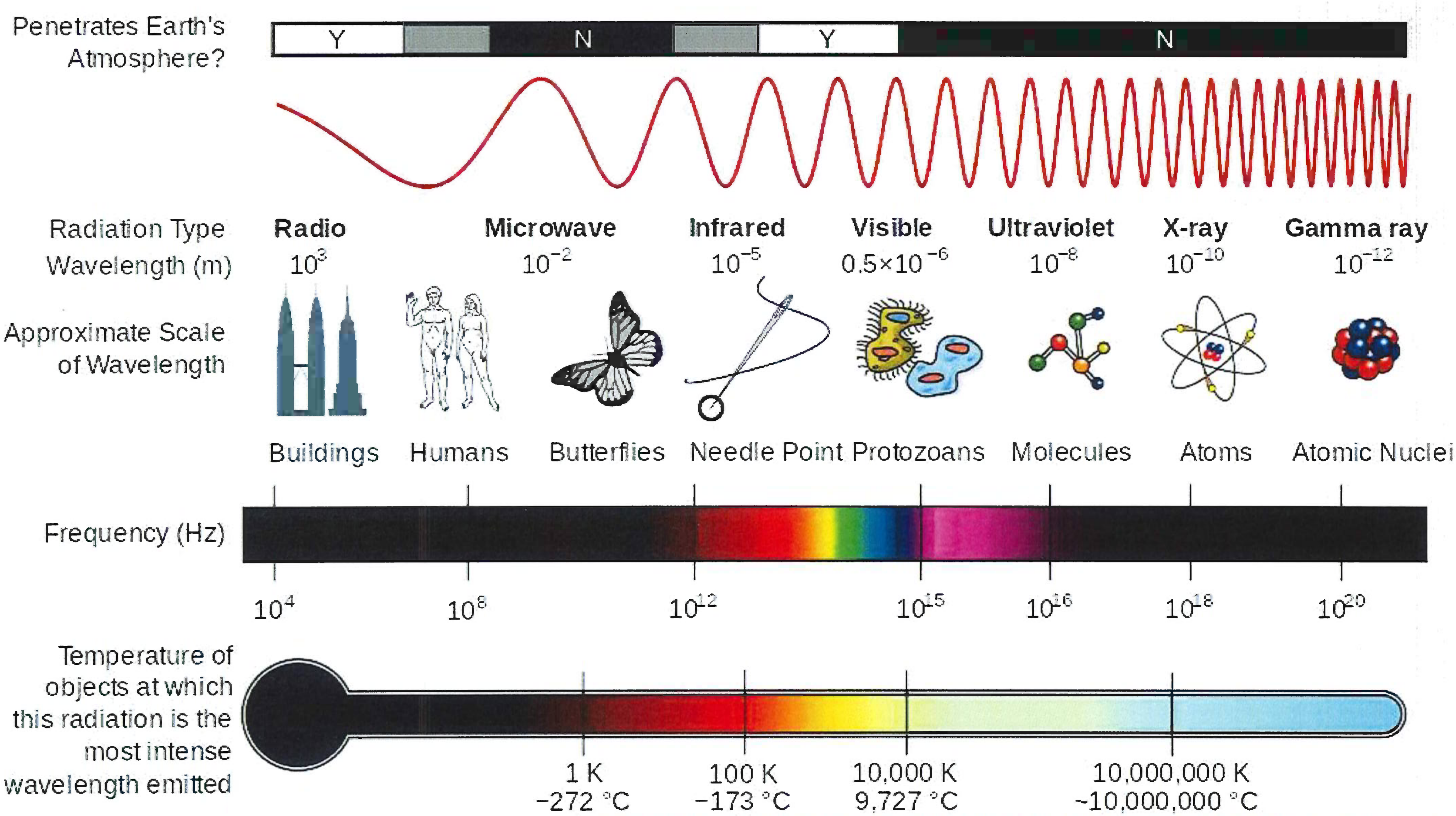
For each $\vec{k} = (k_x, k_y, k_z)$, two ~~g~~ degenerate energy levels with different polarization



$$\lambda_3 = \frac{2L}{3}$$

$$\lambda_2 = \frac{2L}{2}$$

$$\lambda_1 = 2L$$



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