MATH327: StatMech and Thermo

Wednesday, 19 March 2025

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Something to consider

Last month we contrasted gases of distinguishable vs. indist'able particles by counting the ways of labelling particles with different properties (momentum, position, etc.)

What happens if multiple particles have exactly the same properties?

Recap

Grand-canonical ensemble

Will apply to quantum gases → formulate quantum stats

First step: Quantized energy levels ε_ℓ

Plan

Classical Maxwell-Boltzmann statistics

Quantum $\left\{ \begin{matrix} \text{Bose-Einstein} \\ \text{Fermi-Dirac} \end{matrix} \right\}$ statistics

connection

Organize micro-states by N_i

$$Z_g = \sum_i e^{-\beta(E_i - \mu N_i)}$$

$$= \sum_{i,\, N_i = 0} e^{-\beta E_i} + \sum_{j,\, N_j = 1} e^{-\beta(E_i - \mu)} + \sum_{k,\, N_k = 2} e^{-\beta(E_i - 2\mu)} + \dots$$

$$= Z_0 + e^{\beta\mu} Z_1 + e^{2\beta\mu} Z_2 + \dots$$

$$Z_g = \sum_{N=0}^{\infty} \left(e^{\beta\mu}\right)^N Z_N$$

Z_N: N-particle canonical part. func.

"Fugacity" $\xi = e^{\beta\mu} = e^{\mu/T}$

Recall $Z_N = \frac{1}{N!} Z_1^N$ for non-interacting indist'able particles

$\frac{1}{N!}$: corrects for over-counting (no labels)

$$Z_g = \sum_{N=0}^{\infty} \frac{1}{N!} \left(e^{\beta\mu} Z_1\right)^N = \exp\left[e^{\beta\mu} Z_1\right]$$

Single-particle micro-states are just energy levels

$$Z_1 = \sum_{\ell=0}^{L} e^{-\beta E_\ell}$$

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

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

<u>Maxwell-Boltzmann</u> g.c. part. func.

Hidden classical assumption:

$Z_N = \frac{1}{N!} Z_1^N$ iff. all N particles occupy different E_ℓ

Example: $N=2$ particles with $L+1 = 5$ energy levels

How many dist'able micro-states in sum $Z_D = \sum_i (\cdots)$?

page 92 $\boxed{5 \times 5 = 25}$

$\therefore$ for indist'able, $\frac{1}{2!} 25 = \cancel{12.5}$ terms in $Z_I = \sum_i (\cdots)$

Check all dist'able micro-states  = "ROOBO"

$\frac{1}{2} = \frac{1}{N!}$	RB000 ⟷	BR000	BOROO	BOORO	BOOOR
	ROB00	ORB00	OBROO	OBORO	OBOOR
	ROOBO	OROBO	OORBO	OOBRO	OOBOR
	ROOOB	OROOB	OOROB	OOORB ⟷	OOOBR
No $\frac{1}{N!}$	20000	02000	00200	00020	00002

Classical continuous energies
guarantee all particles in different energy levels

True quantum statistics
defining micro-states in terms of how many particles occupy each discrete energy level ε_ℓ

occupation number n_ℓ

Same example:

11000	01100	00110
10100	01010	00101
10010	01001	00011
10001	02000 ×	00020 ×
20000 ×	00200 ×	00002 ×

✓

Z_2 sums over 15 w_i not 12.5

Not all occupation numbers n_ℓ are allowed

Two possibilities (in 3d)

1) $n_\ell = 0, 1, 2, \ldots \rightarrow$ bosons (Higgs, photons, pions, He4)

2) $n_\ell = 0$ or $n_\ell = 1 \rightarrow$ fermions (electrons, protons, He3)

"Pauli exclusion principle" → chemistry, life

Same example: Only 10 w_i for fermions page 34

Different allowed micro-states → different quantum statistics

Grand-canonical part. func. for bosons

sum $n_\ell = 0, 1, 2, \cdots$ for every energy level ε_ℓ

Warm-up: Single ε_0 with energy E_0

page 95 $\boxed{\text{Micro-state energy } E_i = N_i E_0 = n_0 E_0}$

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

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

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

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

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

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

$\{n_\ell\}$ defines micro-state w_i

$$Z_g = \sum_{n_0} \sum_{n_1} \cdots \sum_{n_\mathcal{L}} \exp[-\beta(E_i - \mu N_i)]$$

Non-interacting particles: $E_i = \sum_\ell n_\ell E_\ell$

$N_i = \sum_\ell n_\ell$

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

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

$$= \prod_{\ell=0}^{\mathcal{L}} \frac{1}{1 - e^{-\beta(E_\ell - \mu)}} \qquad E_\ell > \mu$$

"Factorization"

Bose-Einstein g.c. part. func.

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

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

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

<u>Fermi-Dirac</u> g.c. part. ~~M~~ func.

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

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

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

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

Classical MB should emerge from quantum when $\langle N\rangle \ll$ # of <u>accessible</u> energy levels

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

Let's compute $\langle N\rangle = -\frac{\partial}{\partial\mu}\Phi$ for all three and check high T

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

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All occupation numbers ≥ 0 ✓

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

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

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 <u>both</u>

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

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

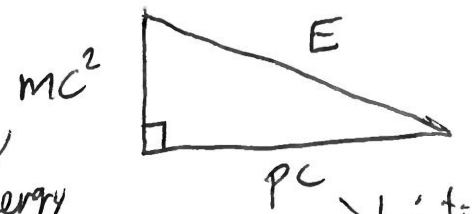
with $-\mu \gg T \gg E_\ell$ so $e^{\beta(E_\ell - \mu)} \gg 1$

Preview: Quantum gases

Need to specify energy levels ε_ℓ ~~and~~ and energies E_ℓ

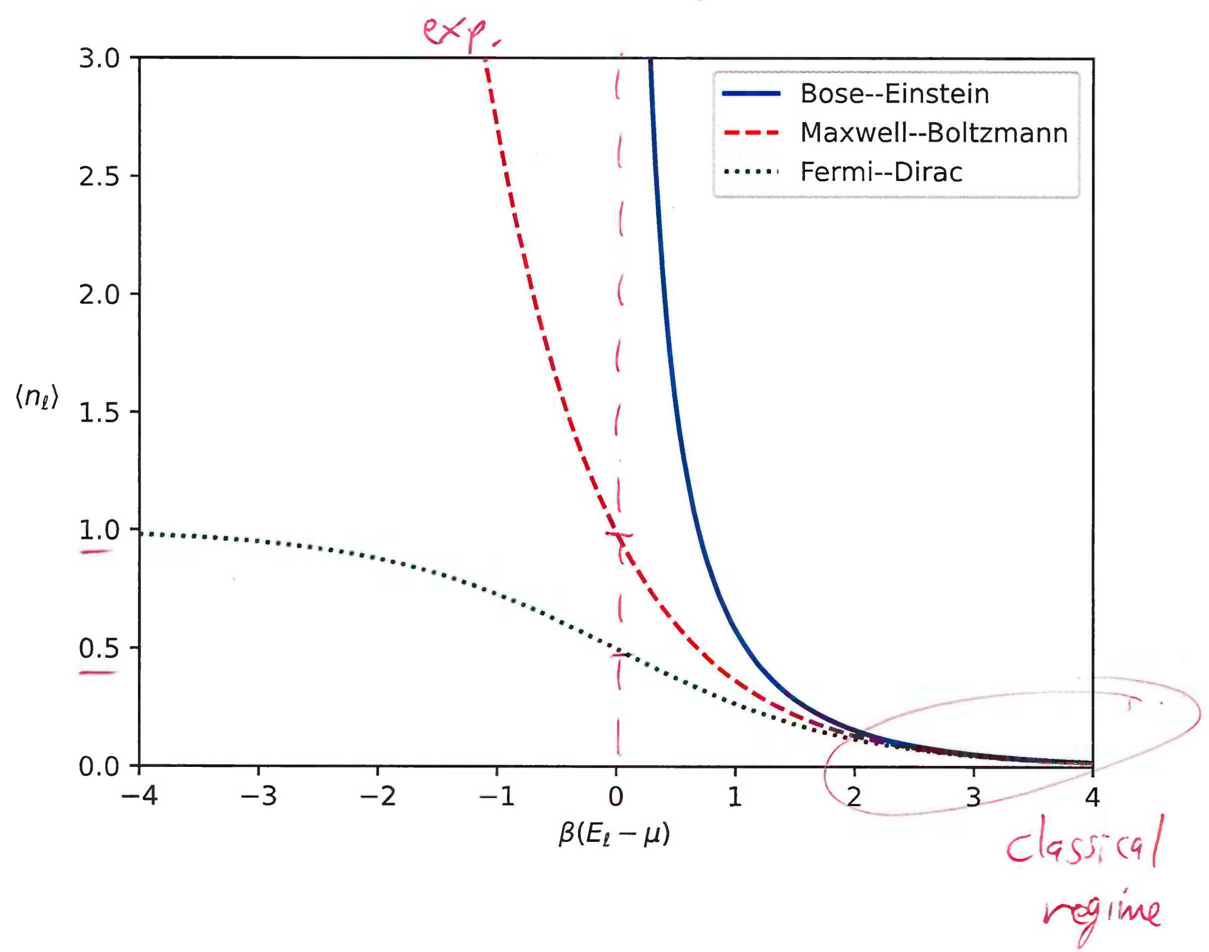
In general $E^2 = (mc^2)^2 + (pc)^2$ $\qquad p^2 = p_x^2 + p_y^2 + p_z^2$

"Einstein's triangle"



mass energy (Fixed)

kinetic energy


exp.
3.0
2.5
2.0
1.5
1.0
0.5
0.0
⟨n_ℓ⟩
−4
−3
−2
−1
0
1
2
3
4
β(E_ℓ − μ)
Bose--Einstein
Maxwell--Boltzmann
Fermi--Dirac
classical regime