MATH327: StatMech and Thermo

Tuesday, 17 March 2026

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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

Generalized therm. identity

$$dE = T\,dS - P\,dV + \mu\,dN$$

$$\rightarrow \mu = \left.\frac{\partial E}{\partial N}\right|_{V,S} < 0$$

Quantized energy levels ε_ℓ $\quad \ell = 0, 1, \ldots \mathcal{L}$

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

Today

Classical Maxwell-Boltzmann statistics

Quantum ~~Bose-Einstein~~ statistics

For Z_1, sum over single micro-state for each ε_ℓ

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

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

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

<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 ε_ℓ

~~Exact~~ Guaranteed by classical ~~at~~ continuous energies

Breaks down when relatively few ε_ℓ with non-negligible $e^{-\beta E_\ell}$

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

How many micro-states in sums $Z_D = \sum_i (\ldots)$ and $Z_I = \sum_i (\ldots)$?

$\boxed{5\times 5 = 25 \text{ for } Z_D \to \frac{1}{2!}25 = \cancel{12.5} \text{ indist'able micro-states}}$

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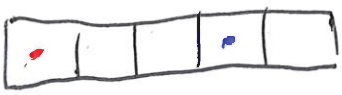
Check all dist'able micro-states

 = "ROOBO"

RBOOO ⟷	BROOO	BOROO	BOORO	BOOOR
ROBOO	ORBOO	OBROO	OBORO	OBOOR
ROOBO	OROBO	OORBO ⟷	OOBRO	OOBOR
ROOOB	OROOB	OOROB	OOORB ⟷	OOOBR
2OOOO	O2OOO	OO2OO	OOO2O	OOOO2

$\frac{1}{2} = \frac{1}{N!}$

No $1/N!$

For $N \gg 1$ would be nightmare to track all multiple-occupancy overcounting factors

True quantum statistics

defines micro-states in terms of how many particles occupy each discrete energy level ε_ℓ

occupation number n_ℓ

Same example:

1 1 0 0 0	0 1 1 0 0	0 0 1 1 0
1 0 1 0 0	0 1 0 1 0	0 0 1 0 1
1 0 0 1 0	0 1 0 0 1	0 0 0 1 1
1 0 0 0 1	0 2 0 0 0 ×	0 0 0 2 0 ×
2 0 0 0 0 ×	0 0 2 0 0 ×	0 0 0 0 2 ×

$\therefore$ Z_I sums over 15 w_i not 12.5 ✓

$(\#(\#+1))/2 = ((\ell+1)(\ell+2)/2)$

Not all occupation numbers n_ℓ are allowed

Two possibilities (in 3d)

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

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

"Pauli exclusion principle" → chemistry, life

(Not repulsion – feature of quantum physics)

Same example: Only 10 w_i for fermions

$(\#(\#-1)/N) = ((\ell+1)\ell/2)$

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Different allowed micro-states → different quantum statistics