MATH327: Statistical Physics

Friday, 22 March 2024

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Something to consider

A few weeks ago we contrasted systems of distinguishable and indistinguishable particles by counting the ways of labelling particles with different properties (momentum, position, etc.)

What happens if multiple particles have exactly the same properties?

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

Grand-canonical potential $\Phi = -T \log Z_g$ $\qquad P_i = \frac{1}{Z_g} e^{-\beta(E_i - \mu N_i)}$

Derivatives of $\Phi \to S(T,\mu)$, $\langle E\rangle(T,\mu)$, $\langle N\rangle(T,\mu)$

$$\frac{\partial}{\partial \mu}\Phi = \frac{-1}{\beta Z_g}\frac{\partial Z_g}{\partial \mu} = \frac{-1}{\beta Z_g}\sum_i \frac{\partial}{\partial \mu} e^{-\beta(E_i - \mu N_i)}$$

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

$$= -\sum_i P_i N_i \cancel{= \langle N\rangle}$$

$$= -\langle N\rangle$$

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$$\frac{\partial}{\partial T}\Phi = -\log Z_g - T\frac{\partial}{\partial T}\log Z_g \qquad \frac{\partial}{\partial T} = -\beta^2\frac{\partial}{\partial \beta}$$

$$-T(-\beta^2)\frac{1}{Z_g}\sum_i \frac{\partial}{\partial \beta} e^{-\beta(E_i - \mu N_i)} = \frac{-1}{T}\sum_i P_i(E_i - \mu N_i) = \frac{-\langle E\rangle + \mu\langle N\rangle}{T}$$

$$\frac{\partial}{\partial T}\Phi = -\log Z_g - \left(\frac{\langle E\rangle - \mu\langle N\rangle}{T}\right) = \frac{\Phi - \langle E\rangle + \mu\langle N\rangle}{T}$$

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$$S = -\sum_i p_i \log p_i = -\sum_i p_i \log\left(\frac{1}{Z_g} e^{-\beta(E_i - \mu N_i)}\right)$$

$$= \log Z_g + \beta\langle E\rangle - \beta\mu\langle N\rangle$$

$$= \frac{-\Phi + \langle E\rangle - \mu\langle N\rangle}{T} = -\frac{\partial}{\partial T}\Phi$$

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Collecting results

$$\langle N\rangle = -\frac{\partial}{\partial \mu}\Phi \qquad S = -\frac{\partial}{\partial T}\Phi$$

$$\langle E\rangle = T^2 \frac{\partial}{\partial T}\log Z_g + \mu\langle N\rangle = -T^2\frac{\partial}{\partial T}\left(\frac{\Phi}{T}\right) + \mu\langle N\rangle$$

$$\Phi = -TS + \langle E\rangle - \mu\langle N\rangle$$

Generalized first law

Recall canonical $\quad dE = Q + W = TdS - PdV$

Now dN possible as well

Expand $\quad dS = \left.\frac{\partial S}{\partial E}\right|_{V,N} dE + \left.\frac{\partial S}{\partial V}\right|_{E,N} dV + \left.\frac{\partial S}{\partial N}\right|_{V,E} dN$

$$= \frac{1}{T}dE + \underbrace{\left.\frac{\partial S}{\partial V}\right|_{E,N}}_{T} dV - \frac{\mu}{T}dN$$

Fixed $N \to$ canonical

Fixed $E \to dE = TdS - PdV = 0$

$$\frac{\partial S}{\partial V} = \frac{P}{T}$$

Result: "Generalized thermodynamic identity"

$$dE = TdS - PdV + \underbrace{\mu dN}_{\text{"chemical work"}}$$

Fix N and V: $dE = T\,dS \rightarrow \frac{1}{T} = \frac{\partial S}{\partial E}\Big|_{N,V}$ ✓

Fix N and S: $dE = -P\,dV \rightarrow p = -\frac{\partial E}{\partial V}\Big|_{N,S}$ ✓

Fix S and V: $dE = \mu\,dN \rightarrow \mu = \frac{\partial E}{\partial N}\Big|_{S,V}$

Recall $\Delta N > 0$ with fixed E naturally increases S

$\rightarrow$ reduce E to keep S fixed $(T > 0)$

$\rightarrow$ $\mu < 0$ for natural systems ✓

Quantum statistics

Recall ideal gas regularization

Discrete momenta $\rightarrow$ energy levels with spacing $\frac{\Delta E}{T} \propto \frac{\hbar^2}{mTL^2}$

Sums $\rightarrow$ integrals in limit of continuous momenta

Now stick with discrete energy levels

Will give classical (non-quantum) Maxwell-Boltzmann statistics

and reveal what is needed for true quantum statistics

Label energy levels as $\mathcal{E}_\ell$ with energy E_ℓ

Can have $E_m = E_n$ for $\mathcal{E}_m$ and $\mathcal{E}_n$ $m \neq n$

$\vec{p} = \frac{\hbar\pi}{L}(1,0,0)$ vs. $\frac{\hbar\pi}{L}(0,0,1)$

"Degenerate" energy levels

Label $E_m \leq E_n$ for $m < n$ and $E_\ell \geq E_0 \geq 0$

Organize micro-states by N_i

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

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

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

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

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 (ideal) systems

correct for over-counting indist'able particles

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

Single-particle micro-states: Occupy each energy level

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

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

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

<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

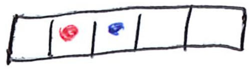
Example: $N=2$ particles, $E_\ell = 0$ for all $L+1 = 5$ energy levels

↳ Z_N count micro-states

$$Z_1 = \sum_{\ell=0}^{4} e^{-\beta E_\ell} = \sum_{\ell=0}^{4} 1 = 5$$

Z_N counts ways to place N balls in $L+1$ boxes

Let $N=2$ particles be dist'able



$$Z_D = 25 = Z_1^2$$

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For indist'able $Z_I = \frac{1}{N!} Z_1^N = \frac{1}{2} 25 = 12.5$ micro-states

can't be right

Check all 25 dist'able micro-states

$\frac{1}{2} = \frac{1}{N!}$	RB000 ⟷	BR000	B0R00	B00R0	B000R
	R0B00	0RB00	0BR00	0B0R0	0B00R
	R00B0	0R0B0	00RB0	00BR0	00B0R
	R000B	0R00B	00R0B	000RB ⟷	000BR
No $\frac{1}{N!}$ →	20000	02000	00200	00020	00002

Classical continuous energies
guarantee all particles in different energy levels

True <u>quantum statistics</u>
defines micro-states in terms of <u>how many particles</u>
occupy each discrete energy levels E_ℓ

occupation number n_ℓ

Back to example of $N=2$ with $L+1=5$ (and γ E_ℓ)

How many micro-states to sum to get part. func.?

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

Z_2 sums over 15 w_i not 12.5 ✓

~~Thus~~

Not all occupation number n_ℓ are allowed

Two possibilities (3d)

1) Bosons can have $n_\ell = 0, 1, 2, 3 \ldots$ (Higgs, photons, ...)

2) Fermions can have $n_\ell = 0$ or $n_\ell = 1$ only (electrons, protons, ...)

"Pauli exclusion principle"

↳ chemistry, life

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Back to $N=2$ example: only 10 w_i for fermions

Different allowed micro-states → different ~~quantities~~ quantum statistics