MATH327: StatMech and Thermo

Monday, 17 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

Heat engine efficiency

Grand-canonical ensemble - Fix T

Grand-canonical partition function

$$Z_g = \sum_i \exp[-\beta(E_i - \mu N_i)]$$

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

Today

Grand-canonical predictions

Quantum statistics

From Z_g predict

Entropy $\quad S(T,\mu) = -\sum_i p_i \log p_i$

Internal energy $\quad \langle E \rangle = \sum_i p_i E_i = \frac{1}{Z_g} \sum_i E_i e^{-\beta(E_i - \mu N_i)}$

Particle number $\quad \langle N \rangle = \frac{1}{Z_g} \sum_i N_i e^{-\beta(E_i - \mu N_i)}$

All related to derivatives of the <u>grand-canonical potential</u> ("Landau free energy")

$$\Phi(T,\mu) = -T \log Z_g$$

$$Z_g = e^{-\Phi/T}$$

$$p_i = e^{\beta(\Phi - E_i + \mu N_i)}$$

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

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

$$= \cancel{\mu} - \langle N\rangle$$

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

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

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

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

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

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

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

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Collecting results:

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

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

$$\Phi = -T\cdot S + \langle E\rangle - \mu\langle N\rangle$$

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

Generalize to account for dN

Convenient to expand entropy

$$dS = \frac{\partial S}{\partial E}\bigg|_{N,V} dE + \frac{\partial S}{\partial V}\bigg|_{E,N} dV + \frac{\partial S}{\partial N}\bigg|_{V,E} dN$$

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

↳ Fix N → canonical

Fix E: $dE = T\,dS - PdV = 0$

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

Result: Generalized thermodynamic identity

$$dE = T\,dS - PdV + \mu dN$$

"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: $dE = -PdV \rightarrow P = \frac{-\partial E}{\partial V}\Big|_{N,S}$ ✓

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

∴ reduce E to keep S fixed $(T > 0)$

→ $\mu < 0$ for natural systems ✓

Quantum statistics

Recall ideal gas regularization:

continuous → discrete E → continuous with $\frac{L}{2\pi\hbar}$

First step: Keep quantized energy levels

→ classical (non-quantum) Maxwell-Boltzmann statistics

Will reveal what is needed for true quantum statistics

Label energy levels as ε_ℓ with energy E_ℓ

Can have "degenerate" $E_m = E_n$ for $\varepsilon_m \neq \varepsilon_n$

Ex: $\vec{p} = (1,0,0)$ vs. $(0,1,0)$ vs. $(0,0,1)$

Choose $E_m \leq E_n$ for $m < n$

and $0 \leq E_0 \leq E_\ell$