MATH327: StatMech and Thermo

Thursday, 12 March 2026

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Something to consider

We motivated $\mu < 0$ so that particles flow analogously to heat.

Is there a more direct way to justify $\mu < 0$ being natural like $T > 0$?

Recap

Fridges and heat pumps, COPs

Grand-canonical ensemble

Chemical potential $\mu = -T \left.\frac{\partial S}{\partial N}\right|_E$

Today

Grand-canonical partition function

$\rightarrow$ predict S, $\langle E \rangle$, $\langle N \rangle$

E_i and N_i depend on micro-state ω_i

Want p_i free from dependence on reservoir

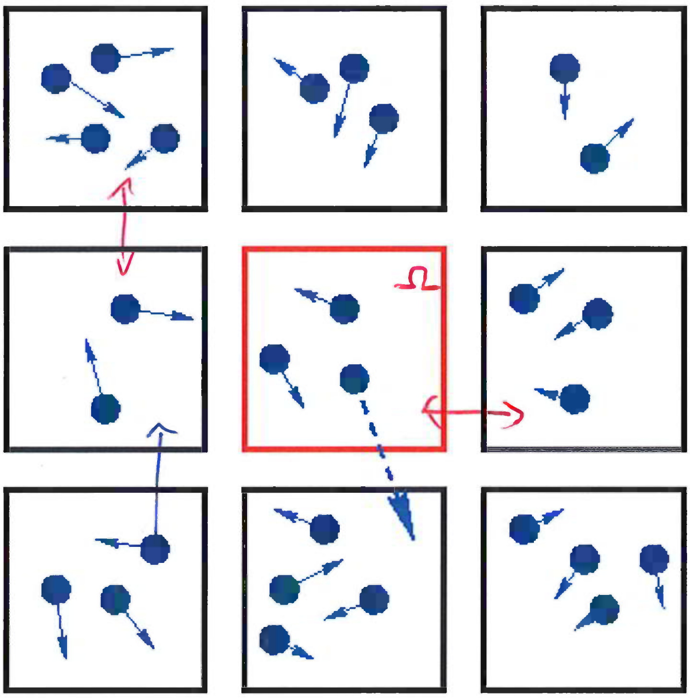
Adapt replica trick

$$E_{tot} = E + E_{res} = \sum_{r=1}^{R} E_r$$

$$N_{tot} = N + N_{res} = \sum_r N_r$$

Say Ω has M micro-states $\omega_i = \omega_1, \omega_2, \ldots \omega_M$ with energy E_i and N_i indist'able particles

$\Omega_{tot} = \Omega \otimes \Omega_{res} \rightarrow R$ copies of Ω



Recall occupation numbers n_i and probabilities $p_i = n_i/R$

replica in w_i

$$\sum_{i=1}^{M} n_i = R$$

$$\sum_i p_i = 1$$

$$E_{tot} = \sum_i E_i n_i \qquad N_{tot} = \sum_i N_i n_i = R \sum_i N_i p_i$$

Compute T and μ of micro-canonical Ω_{tot}
(intensive)

Need therm. equil. $\rightarrow$ maximize S with constraints

Same $M_{tot} = \binom{R}{n_1}\binom{R-n_1}{n_2} \cdots = \dfrac{R!}{n_1! n_2! \cdots n_M!} \qquad n_i \gg 1$

$$S_{tot} = -R \sum_i p_i \log p_i$$

Different w_i $\rightarrow$ additional Lagrange multiplier

$$\bar{S} = -R \sum_i p_i \log p_i + \alpha\left(\sum_i p_i - 1\right) - \beta\left(R \sum_i E_i p_i - E_{tot}\right)$$
$$+ \gamma\left(R \sum_i N_i p_i - N_{tot}\right)$$

$$\frac{\partial \bar{S}}{\partial p_k} = 0 = -R(\log p_k + 1) + \alpha - \beta R E_k + \gamma R N_k$$

$$\log p_k = -1 + \frac{\alpha}{R} - \beta E_k + \gamma N_k$$

$$p_k = \frac{\exp(-\beta E_k + \gamma N_k)}{\exp\left(1 - \frac{\alpha}{R}\right)} = \frac{1}{Z_g} e^{-\beta E_k + \gamma N_k}$$

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Impose constraints:

$$\boxed{1 = \sum_i p_i = \frac{1}{Z_g} \sum_i e^{-\beta E_i + \gamma N_i} \qquad Z_g = \sum_i e^{-\beta E_i + \gamma N_i} = Z_g(\beta, \gamma)}$$

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grand-canonical partition func.

T and μ come from entropy

$$S_{tot} = -R \sum_i p_i \log\left(\frac{1}{Z_g} e^{-\beta E_i + \gamma N_i}\right)$$

$$= -R \sum_i p_i \left(-\log Z_g - \beta E_i + \gamma N_i\right)$$

$$= R \log Z_g + \beta E_{tot} - \gamma N_{tot}$$

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$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = R\left(\frac{\partial \beta}{\partial E} \frac{\partial}{\partial \beta} \overset{(i)}{\log Z_g} + \frac{\partial \gamma}{\partial E} \frac{\partial}{\partial \gamma} \overset{(ii)}{\log Z_g}\right)$$

$$+ \beta + E \frac{\partial \beta}{\partial E} - N \frac{\partial \gamma}{\partial E}$$

i) $\frac{1}{Z_g} \sum_i \frac{\partial}{\partial \beta} e^{-\beta E_i + \gamma N_i} = \frac{1}{Z_g} \sum_i (-E_i) e^{-\beta E_i + \gamma N_i}$

$$= -\sum_i E_i p_i = \frac{-E}{R}$$

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ii) $\frac{1}{Z_g} \sum_i \frac{\partial}{\partial \gamma} e^{-\beta E_i + \gamma N_i} = \sum_i N_i p_i = \frac{N}{R}$

$$\frac{1}{T} = -E \cancel{\frac{\partial \beta}{\partial E}} + N \cancel{\frac{\partial \gamma}{\partial E}} + \beta + E \cancel{\frac{\partial \beta}{\partial E}} - N \cancel{\frac{\partial \gamma}{\partial E}} = \beta \checkmark$$

$$-\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_E = R\left(\frac{\partial \beta}{\partial N} \cancel{\left(\frac{-E}{R}\right)} + \frac{\partial \gamma}{\partial N} \cancel{\left(\frac{N}{R}\right)}\right) + E \cancel{\frac{\partial \beta}{\partial N}} - \gamma - N \cancel{\frac{\partial \gamma}{\partial N}}$$

$$\gamma = \mu / T$$

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We have derived the micro-state probabilities

$$P_i = \frac{1}{Z_g} e^{-E_i/T + \mu N_i/T} = \frac{1}{Z_g} e^{-\beta(E_i - \mu N_i)}$$

$$Z_g(T, \mu) = \sum_i e^{-(E_i - \mu N_i)/T}$$

Both E_i and N_i fluctuate

Particle reservoir unknowable apart from fixing T and μ

From Z_g predict

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

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

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

All related to derivatives of the <u>grand-canonical potential</u>

("Landau free energy")

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

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

$$P_i = \exp[\beta(\Phi - E_i + \mu N_i)]$$

$$\boxed{\begin{aligned}\frac{\partial}{\partial\mu}\Phi &= \frac{-1}{\beta Z_g}\frac{\partial Z_g}{\partial\mu} = \frac{-1}{\beta Z_g}\sum_i \frac{\partial}{\partial\mu} e^{-\beta(E_i - \mu N_i)} \\ &= \frac{-\cancel{\beta}}{\beta Z_g}\sum_i N_i e^{-\beta(E_i - \mu N_i)} = -\sum_i N_i P_i = -\langle N \rangle\end{aligned}}$$

$$\frac{\partial}{\partial T}\Phi = -\log Z_g - \underline{\frac{1}{\beta Z_g}\frac{\partial Z_g}{\partial T}} \qquad \frac{\partial}{\partial T} = -\beta^2 \frac{\partial}{\partial \beta}$$

$$+\frac{\beta^2}{\beta Z_g}\frac{\partial Z_g}{\partial \beta} = \frac{\beta}{Z_g}\sum_i \frac{\partial}{\partial \beta} e^{-\beta(E_i - \mu N_i)}$$

$$= \frac{-1}{T}\sum_i (E_i - \mu N_i) p_i = \frac{-\langle E\rangle + \mu\langle N\rangle}{T}$$

$$= -T\frac{\partial}{\partial T}\log Z_g$$

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

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

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

Collect results:

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

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

$$= \frac{\partial}{\partial \beta}(\beta\Phi) + \mu\langle N\rangle$$

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

Recall canonical $dE = Q + W = T\,dS - P\,dV$

Generalize to account for dN

Convenient to expand entropy

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

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

Fix $N \rightarrow$ canonical

Fix $E \rightarrow dE = 0 = TdS - PdV$

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

Result: Generalized thermodynamic identity

$$dE = TdS - PdV + \mu dN$$

"chemical work"

Fix N and V: $dE = TdS$

$$\rightarrow \frac{1}{T} = \frac{\partial S}{\partial E}\Big|_{N,V} \quad ✓$$

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

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

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

Quantum statistics

p_i, Z_g and w_i

Recall ideal gas regularization

continuous $\vec{p}$ and E $\rightarrow$ discrete $\rightarrow$ continuous with $\frac{L}{2\pi\hbar}$

First step: Keep quantized energy levels

$\longrightarrow$ classical (non-quantum) Maxwell-Boltzmann statistics

Will reveal second step needed for true quantum statistics

Label energy levels as ε_ℓ with energy E_ℓ (not E_i for w_i)

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

Example: $\vec{p} \propto \vec{k} = (1,0,0)$ vs. $(0,1,0)$ vs. $(0,0,1)$

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

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

Organize micro-states by N_i

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

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

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

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

Z_N: N-particle canonical part. func.

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

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

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

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

Express in terms of energy levels...