Tue 19 Mar

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Grand-canonical ensemble

Particle reservoir fixes T

and chemical potential $\mu = -T \frac{\partial S}{\partial N}\Big|_E$

particles flow to smaller μ

N_i and E_i can change for differents micro-states w_i

Want p_i free from dependence on reservoir

Adapt replica trick

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

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

Ω has M micro-states $w_i = w_1, w_2, \dots w_M$

with energy E_i and N_i particles (indist'able)

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

replicas in w_i

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

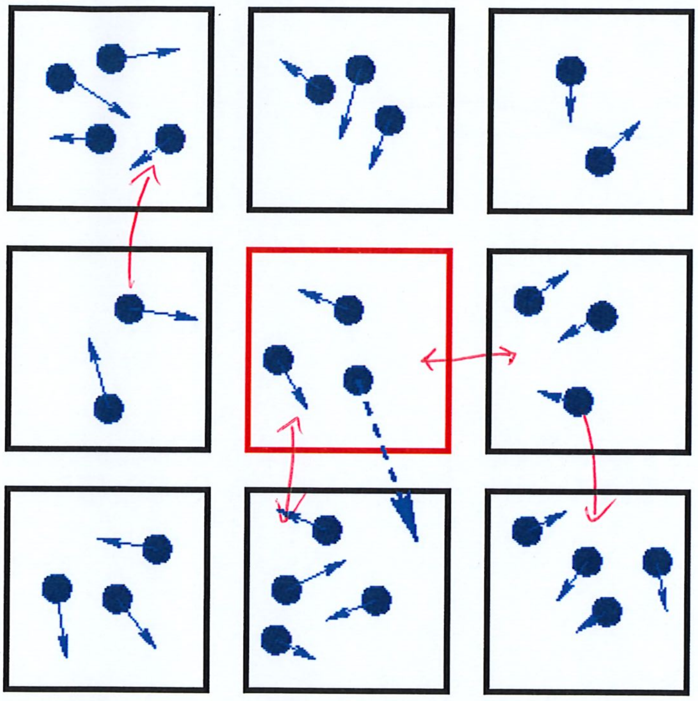
$$\sum_i p_i = 1$$

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

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

Need therm. equilibrium $\rightarrow$ maximize S_{tot} with constraints

$$\underbrace{\Omega_{tot}}_{\text{micro-canonical}} = \Omega \otimes \overbrace{\Omega_{res}}^{R-1 \gg 1 \text{ copies}} \rightarrow R \text{ copies of } \Omega$$



Same $M_{tot} = \binom{R}{n_1}\binom{R-n_1}{n_2}\binom{R-n_1-n_2}{n_3}\cdots = \frac{R!}{n_1!\, n_2! \cdots n_M!}$

$$S_{tot} = -R \sum_i p_i \log p_i \qquad n_i \gg 1$$

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

$$\boxed{\begin{aligned} \frac{\partial \bar{S}}{\partial p_k} &= 0 = -R(\log p_k + 1) + \alpha - \beta R E_k + \gamma R N_k \\ \log p_k &= -1 + \frac{\alpha}{R} - \beta E_k + \gamma N_k \\ p_k &= \frac{\exp(-\beta E_k + \gamma N_k)}{\exp\left(1 - \frac{\alpha}{R}\right)} = \frac{1}{Z_g} e^{-\beta E_k + \gamma N_k} \end{aligned}}$$

page 83

Impose constraint

$$\boxed{\begin{aligned} 1 &= \sum_i p_i = \frac{1}{Z_g} \sum_i e^{-\beta E_i + \gamma N_i} \\ Z_g(\beta, \gamma) &= \sum_{i=1}^{M} e^{-\beta E_i + \gamma N_i} \end{aligned}}$$

page 84

grand-canonical partition function

T and μ come from entropy

$$\boxed{\begin{aligned} S_{tot} &= -R \sum_i p_i \log\left(\frac{1}{Z_g} e^{-\beta E_i + \gamma N_i}\right) \\ &= -R \sum_i p_i \left(-\log Z_g - \beta E_i + \gamma N_i\right) \\ &= R \log Z_g + \beta E_{tot} - \gamma N_{tot} \end{aligned}}$$

page 84

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

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

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

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

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

page 85

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

$$\beta = \frac{1}{T}$$

$$\frac{-\mu}{T} = \frac{\partial S}{\partial N}\Big|_E = R\left(\frac{\partial \beta}{\partial N}\cancelto{-E/R}{\frac{\partial}{\partial \beta}\log Z_g} + \frac{\partial \gamma}{\partial N}\cancelto{N/R}{\frac{\partial}{\partial \gamma}\log Z_g}\right)$$

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

page 85

so $\gamma = \mu/T$

Putting things together, we have derived the micro-state probabilities

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

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

Both E_i and N_i fluctuate

Reservoir unknowable apart from fixing T and μ

Next step:

Start with Z_g

Derive quantities of interest

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

Internal energy $\langle E\rangle(T,\mu) = \sum_i p_i E_i$

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

Particle number $\langle N\rangle(T,\mu) = \sum_i p_i N_i$

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

All related to derivatives of grand-canonical potential

(in therm equil)

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

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

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

"Landau free energy"