Canonical Ensemble - Part 3

Now for more states, 1 thing that could happen is multiple states at diff energy levels, as on midterm

Then if $\Omega(\varepsilon)$ is number of states at that level, saw

$$Q = \sum_{i=1}^{M} e^{-\beta \varepsilon_i} = \sum_{\varepsilon_i} \omega(\varepsilon_i) e^{-\beta \varepsilon_i}$$

In the case where there are ∞ energy

$$Q = \sum_{n=0}^{\infty} \omega(\varepsilon_n) e^{-\beta \varepsilon_n}$$

If very close together, could approx by even spacing, and

$$\varepsilon_n = \varepsilon_0 + n \Delta \varepsilon$$

$$Q \approx \frac{1}{\Delta \varepsilon} \sum_{n=0}^{\infty} \omega(\varepsilon_n) e^{-\beta \varepsilon_n} \Delta \varepsilon$$

$\lim_{\Delta \varepsilon \to 0}$

laplace transform

$$\Rightarrow Q(V,T) \approx \frac{1}{d\varepsilon} \int d\varepsilon\, w(\varepsilon) e^{-\beta \varepsilon}$$

Can use this to solve problems about particles in space if know energy

$d\varepsilon$ or other consts don't effect most properties, b/c derivative of $\ln Q$ for most properties, so constants don't matter

could say $Z = \int d\varepsilon\, w(\varepsilon) e^{-\beta\varepsilon}$

and $\frac{\partial \ln Z}{\partial x} = \frac{\partial \ln Q}{\partial x}$

In classical mech

$$\mathcal{E} = \frac{1}{2}mv^2 + u(x) = p^2/2m + u(x)$$

Turns out to get to classical limit of this partition function on x & p space, get

$$Q = \frac{1}{h}\int_{-L}^{L} dx \int_{-\infty}^{\infty} dp\, e^{-\beta \mathcal{E}(x,p)}$$

1d

If ideal gas $u(x) = 0$

and $\int_{-L}^{L} dx = 2L = V$

so $$Q = \frac{V}{h} \cdot \int_{-\infty}^{\infty} e^{-p^2/2mk_BT}\, dp$$

$$= \sqrt{\frac{2\pi m k_B T}{h^2}} \cdot V = V/\Lambda$$

In 3d: $\mathcal{E} = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$ and

$$Q = \frac{1}{h^3} \int dx\,dy\,dz \int dv_x\,dv_y\,dv_z\, e^{-\beta \mathcal{E}(x,v)}$$

$$= V/h^3 \left[\int dx\, e^{-\beta \cdot \frac{1}{2} m v^2} \right]^3 = V/\Lambda^3$$

(return to this)

This is for one particle

Suppose N independent & distinguishable particles & ideal gas

$$\mathcal{E} = \sum_{i=1}^{N} \frac{1}{2} m \vec{v}_i^{\,2}$$

$$e^{-\beta \mathcal{E}(\vec{v}_1, \vec{v}_2, \ldots)} = e^{-\beta \cdot \frac{1}{2} m v_1^2}\, e^{-\beta \frac{1}{2} m v_2^2} \cdot \ldots$$

So $Q_N = Q_1 \cdot Q_1 \cdot Q_1 \cdot \cdots = Q_1^N$

for independent particles

turns out (how?) if indistinguishable

$$Q = \frac{1}{h^{3N} N!} \int d\vec{x}^{3N} \int d\vec{v}^{3N} e^{-\beta \epsilon(\vec{x}, \vec{v})}$$

so $Q_N = \frac{q^N}{N!}$ $\quad q = V/\Lambda^3$

for ideal gas

$$\langle \varepsilon_v \rangle = -\frac{\partial \ln Q_N}{\partial \beta} = -N \frac{\partial \ln q}{\partial \beta}$$

$$= -N \frac{\partial \ln}{\partial \beta}\left[\beta^{-3/2} + \text{stuff}\right]$$

$$= \frac{3}{2} \cdot \frac{N}{\beta} \frac{\partial \beta}{\partial \beta} = \frac{3}{2} N k_B T$$

$$= \frac{3}{2} nRT \quad \star$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_T = -k_B T \frac{\partial \ln Q_N}{\partial V} = \frac{N k_B T}{V}$$

$$pV = N k_B T = nRT \quad \star$$

Other Ensembles

Condense partition functions for other ensembles in the same fashion using Lagrange multipliers

Will just give major results!

from N, V, T to n, p, T

constraints $\sum N_{ij} = A$ ← num in each state

$$\sum_i N_{ij} \varepsilon_i = \varepsilon_{tot}$$

$$\sum_j N_{ij} V_j = V_{tot} \text{ @ each}$$

Each copy changes volume until @ P_{eq}

Result $\Theta(n, p, T) = \sum_{j=1}^{n} \sum_{i=1}^{m} e^{-\beta \varepsilon_i} \cdot e^{-\beta p V_j}$

discrete

m states

n volumes

$$= \sum_{j=1}^{n} e^{-\beta p V_j} Q(N, V_j, T)$$

or more usually

$$\Theta(n, p, T) = \frac{1}{V_0}\int_0^{\infty} dv\, e^{-\beta p v}\, Q(N, v, T)$$

another laplace transform

$$G = -k_B T \ln \Theta(n, p, T)$$

Another ensemble is Grand Canonical

Const (μ, V, T)

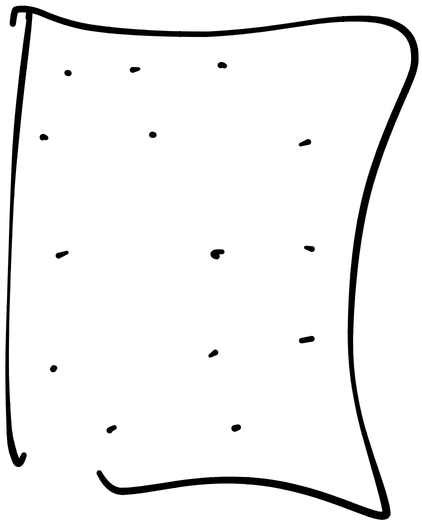
$$\Xi = \sum_{N=0}^{\infty} e^{\beta \mu N}\, Q(N, V, T)$$

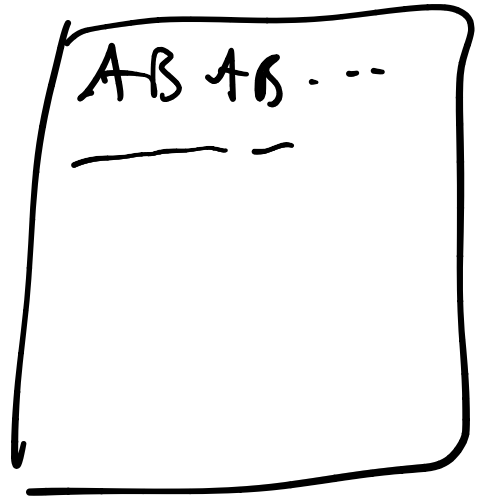
grand pot $\Phi_G = -k_B T \ln \Xi$

Discrete Models Very Valuable
for understanding many chemical processes

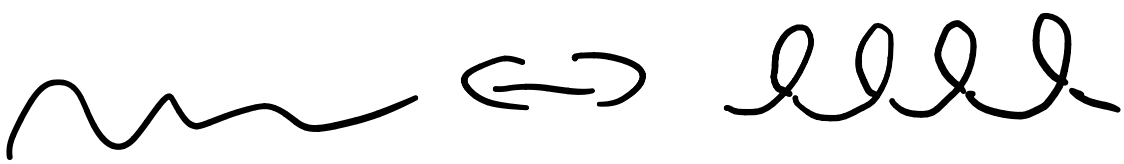
Prev: lattice gas model

phase mixing model





Next time helix coil transition



First: Ising model of magnetization
explains much of phase transition physics