PARTITION FUNCTIONS

When can we write canonical partition function as a simple product of molecular partition functions?

$$Q_{trans} = q_{trans}^{N} \qquad \text{distinguishable particles}$$
$$Q_{trans} = q_{trans}^{N} \big/ N! \qquad \text{indistinguishable particles}$$

These hold when the system microstate energy E_i is a sum of independent molecule energies ε_i (denoted here by ε_{ni} where n_i represent various quantum numbers for molecule i).

$$E_i = \sum_{n_i} \varepsilon_{n_i} = \varepsilon_{n_1} + \varepsilon_{n_2} + \cdots + \varepsilon_{n_N}$$

Then the sum over system microstate energies is just a sum over all the possible combinations of molecular energies ε_1, ε_2, …, ε_N

$$Q = \sum_i e^{-E_i/kT} = \sum_{n_1}\sum_{n_2}\cdots\sum_{n_N} e^{-\left(\varepsilon_{n_1}+\varepsilon_{n_1}+\cdots+\varepsilon_{n_N}\right)/kT}$$
$$= \left(\sum_{n_1} e^{-\varepsilon_{n_1}/kT}\right)\left(\sum_{n_2} e^{-\varepsilon_{n_2}/kT}\right)\cdots\left(\sum_{n_N} e^{-\varepsilon_{n_N}/kT}\right) = q_1 q_2 \cdots q_N = q^N$$

And for indistinguishable particles 1/N! corrects for overcounting.

So if system energy = sum over individual molecular energies ⇒
Canonical partition function = product of molecular partition functions

Same approach justifies writing the molecular partition function as a product of separate partition functions for individual degrees of freedom.

If molecular energy = sum of independent energy terms ⇒
Molecular partition function = product of independent partition functions

e.g. for molecules in the gas phase we have (approximately)

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec} + \ldots \quad \Rightarrow \quad q = q_{trans}\, q_{rot}\, q_{vib}\, q_{elec} \propto$$

For a polymer in a liquid,

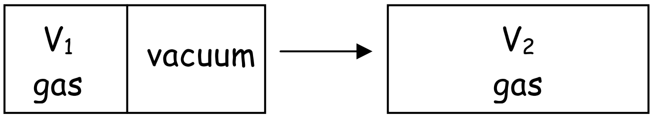
$$\varepsilon \approx \varepsilon_{(\text{everything else})} + \varepsilon_{\text{conf}} \quad \Rightarrow \quad q \approx q_{(\text{everything else})}\, q_{\text{conf}}$$

which means that if there is a largely independent configurational energy contribution, we can calculate q_{conf} and use it to draw conclusions about the likely polymer configurations even if the rest of the polymer energy contributions are hard to calculate quantitatively.

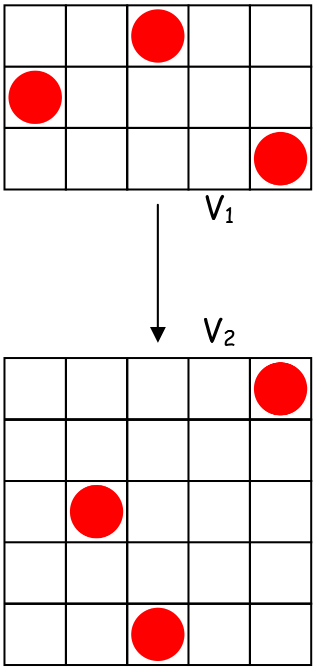
All the thermodynamic functions can be calculated from the canonical partition function. Entropy is directly related to the number of available states.

Examples of macroscopic thermodynamic results
Entropically driven

Free expansion of a gas



"Lattice" model for ideal gas
~ 1 in 1 million lattice sites filled
Total volume V & molecular volume v determine # sites
In this model, all the microstates have = energy
Count # distinguishable system states = degeneracy Ω



$$S = k\ln\Omega \quad \text{gives entropy change}$$

lattice sites = molecular degeneracy ω = V/v = q
because all lattice sites have equal energy $\equiv 0$

ways to place N molecules into lattice sites = $(V/v)^N$ = $\omega^N = q^N$.
distinguishable system microstates = Ω
To avoid overcounting divide by N!

$$\Omega = (V/v)^N/N!$$

If we expand from volume V_1 to V_2, we have

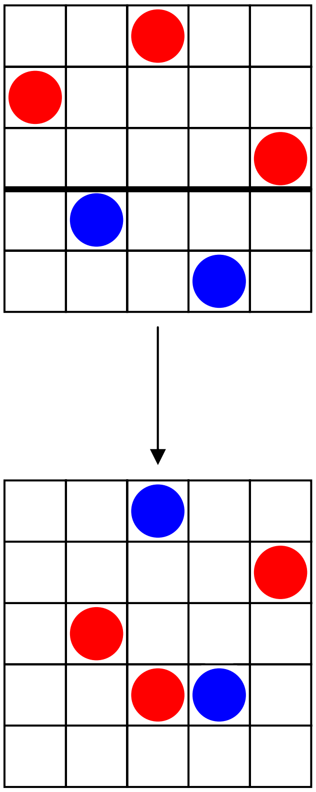
$$\Delta S = k\ln\Omega_2 - k\ln\Omega_1 = k\ln\frac{\Omega_2}{\Omega_1} = k\ln\frac{(V_2/v)^N/N!}{(V_1/v)^N/N!} = Nk\ln\frac{V_2}{V_1} = nR\ln\frac{V_2}{V_1}$$

Should look familiar! And $\Delta G = \Delta H - T\Delta S = -nRT\ln\frac{V_2}{V_1}$

Entropy change is positive, free energy change is negative, as we expect.

Ideal gas mixture

$$\boxed{\begin{array}{c|c} N_A & N_B \\ V_A & V_B \end{array}} \longrightarrow \boxed{\begin{array}{c} N = N_A + N_B \\ V = V_A + V_B \end{array}}$$



Assume same initial (p,T) for A & B
⇒ same (p,T) for mixture
Assume equal molecular volumes & lattice cell sizes.
Then initially

$$S_1 = k\ln\Omega_A + k\ln\Omega_B = k\ln\Omega_A\Omega_B = k\ln\frac{(V_A/v)^{N_A}}{N_A!}\frac{(V_B/v)^{N_B}}{N_B!}$$

After mixing, how many ways to distribute N_A molecules of A and N_B molecules of B among the (V/v) lattice sites?
As before, the number of ways to distribute N molecules among (V/v) sites is $(V/v)^N$. To correct for indistinguishability, this time we divide by $N_A!N_B!$ So the final state entropy is

$$S_2 = k\ln\Omega = k\ln\frac{(V/v)^N}{N_A!N_B!} \quad \text{and}$$

$$\Delta S = S_2 - S_1 = k\ln\frac{(V/v)^N}{N_A!N_B!} - k\ln\frac{(V_A/v)^{N_A}}{N_A!}\frac{(V_B/v)^{N_B}}{N_B!} = k\ln\frac{(V/v)^{(N_A+N_B)}}{(V_A/v)^{N_A}(V_B/v)^{N_B}} = k\ln\frac{V^{N_A}V^{N_B}}{V_A^{N_A}V_B^{N_B}}$$

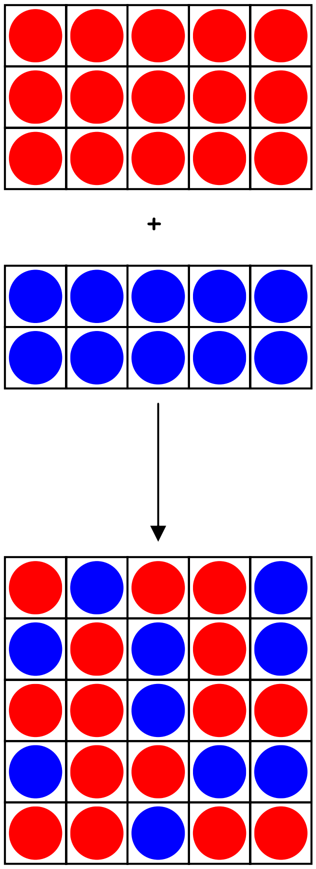
Since the initial pressures are the same, the initial volumes must be in the ratio of the number of molecules, i.e. $V_A/V = N_A/N = X_A$ and $V_B/V = X_B$, so

$$\Delta S = k\ln\frac{V^{N_A}V^{N_B}}{V_A^{N_A}V_B^{N_B}} = -k\ln X_A^{N_A} - k\ln X_B^{N_B} = -Nk\left(X_A\ln X_A + X_B\ln X_B\right) \qquad (>0)$$

With a simple microscopic model we can derive the macroscopic entropy change!

Ideal liquid mixture

Lattice model is different from gas because all the cells are occupied. Then in the pure liquid there is no disorder at all!



$$S_A = k\ln\Omega_A = k\ln 1 = 0$$

$$S_B = k\ln\Omega_B = k\ln 1 = 0$$

Mixture: N molecules for N sites.
First molecule has N choices, second (N – 1), etc.
ways to put the molecules into sites = N!
Correct for overcounting by dividing by $N_A!N_B!$

$$\Delta S_{mix} = S_{mix} - \left(S_A + S_B\right) = S_{mix} = k\ln\Omega_{mix} = k\ln\frac{N!}{N_A!N_B!}$$

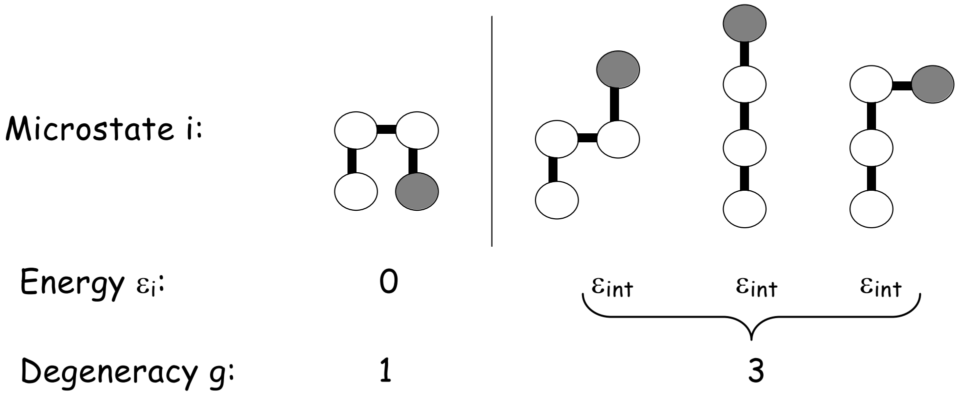
Stirling's approximation $\ln N! \approx N\ln N - N \quad \Rightarrow$

$$\begin{aligned}\Delta S_{mix} &= Nk\ln N - \cancel{Nk} - \left(N_Ak\ln N_A - \cancel{N_Ak} + N_Bk\ln N_B - \cancel{N_Bk}\right)\\ &= (N_A + N_B)k\ln N - N_Ak\ln N_A - N_Bk\ln N_B = N_Ak\ln\frac{N}{N_A} + N_Bk\ln\frac{N}{N_B}\\ &= -Nk\left(X_A\ln X_A + X_B\ln X_B\right)\end{aligned}$$

Note that the lattice model would not work for solid-liquid phase equilibria since it says liquid and crystal have identical (zero) entropy! Really the liquid has many more possible intermolecular configurations in the liquid, molecular rotation, & diffusion – but these occur in both the pure and mixed liquids, so ΔS_{mix} is dominated by the disorder in molecular positions that the lattice model describes reasonably well.

Energy & entropy changes

We saw one example earlier, with 4-segment polymers.



We've redefined the zero of energy as the ground state energy.
"Configurational" molecular partition function is

$$q_{conf} = \sum_{\substack{\text{microstates}\\ i}} e^{-\varepsilon_{i,conf}/kT} = e^{0/kT} + e^{-\varepsilon_{\text{int}}/kT} + e^{-\varepsilon_{\text{int}}/kT} + e^{-\varepsilon_{\text{int}}/kT}$$

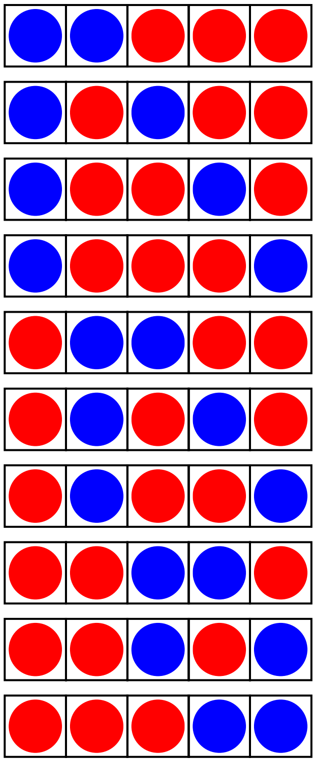
$$= \sum_{\substack{\text{energy levels}\\ \varepsilon_i}} g_{\varepsilon_i} e^{-\varepsilon_i/kT} = e^{0/kT} + 3e^{-\varepsilon_{\text{int}}/kT} = 1 + 3e^{-\varepsilon_{\text{int}}/kT}$$

For a solution of noninteracting polymer molecules,

$$Q_{conf} = q_{conf}^{N}$$

Note no factor of 1/ N! That's for Q_{trans} only. Indistinguishability needs to be accounted for when the molecules are interchanged, i.e. switch positions.

Check this with a system of 5 molecules: 2 of A, 3 of B, in 5 cells. First determine how many distinguishable arrangements there are with all the molecules in the ground state, then with one molecule configurationally excited.



How many distinguishable arrangements?
Ω_{trans} = 5!/2!3! = 10
All the arrangements are shown.

Now imagine one of the two A molecules is in a configurationally excited state with energy e_{conf}. For each of the 10 arrangements, there are now two possibilities – one or the other A molecule is excited, and they are distinguishable based on location! So there are 20 total combinations.

$\Omega_{trans}\,\Omega_{conf} = 20 \quad \Rightarrow \quad \Omega_{conf} = 2$

No correction by $1/N_A$ for Ω_{conf}

Back to our polymer problem…

$$Q_{conf} = q_{conf}^{N} = \left(1+3e^{-\varepsilon_{\text{int}}/kT}\right)^{N}$$

We can immediately start determining the thermodynamic properties!

$$A_{conf} = -kT\ln Q_{conf} = -NkT\ln\left(1+3e^{-\varepsilon_{\text{int}}/kT}\right) = -NkT\ln\left(1+3e^{-\beta\varepsilon_{\text{int}}}\right)$$

$$U_{conf} = -\left(\frac{\partial \ln Q_{conf}}{\partial\beta}\right)_{V,N} = -N\left(\frac{\partial \ln\left(1+3e^{-\beta\varepsilon_{\text{int}}}\right)}{\partial\beta}\right)_{V,N} = N\frac{3\varepsilon_{\text{int}}e^{-\beta\varepsilon_{\text{int}}}}{1+3e^{-\beta\varepsilon_{\text{int}}}}$$

Energy scales with N: molecules are not interacting with each other so total energy is just a sum of individual molecule energies.
Average energy per molecule is

$$\langle\varepsilon_{conf}\rangle = \frac{U_{conf}}{N} = \frac{3\varepsilon_{\text{int}}e^{-\beta\varepsilon_{\text{int}}}}{1+3e^{-\beta\varepsilon_{\text{int}}}}$$

But we also know $\langle\varepsilon\rangle = \sum_i \varepsilon_i P_i = \dfrac{\sum_i \varepsilon_i e^{-\beta\varepsilon_i}}{q} = \dfrac{0+3\varepsilon_{\text{int}}e^{-\beta\varepsilon_{\text{int}}}}{1+3e^{-\beta\varepsilon_{\text{int}}}}$ Yes! Same result

$$S_{conf} = -\frac{A_{conf}}{T} + \frac{U_{conf}}{T} = k\ln Q_{conf} - \frac{1}{T}\left(\frac{\partial \ln Q_{conf}}{\partial \beta}\right)_{V,N} = Nk\ln\left(1+3e^{-\beta\varepsilon_{\text{int}}}\right) + \frac{N}{T}\frac{3\varepsilon_{\text{int}}e^{-\beta\varepsilon_{\text{int}}}}{1+3e^{-\beta\varepsilon_{\text{int}}}}$$

Also scales with N – sum over individual molecule entropy contributions
Average molecular configurational entropy is

$$s_{conf} = k\ln\left(1+3e^{-\beta\varepsilon_{\text{int}}}\right) + \frac{1}{T}\frac{3\varepsilon_{\text{int}}e^{-\beta\varepsilon_{\text{int}}}}{1+3e^{-\beta\varepsilon_{\text{int}}}}$$

In high-T (low-β) limit, it's $k\ln(4)$ as expected. In low-T limit, it's $k\ln(1) = 0$.

$$\mu_{conf} = \left(\frac{\partial A}{\partial N}\right)_{T,V} = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V} = -kT\ln\left(1+3e^{-\beta\varepsilon_{\text{int}}}\right)$$

Chemical potential is just A per molecule, and A scales with N so it's just A/N.

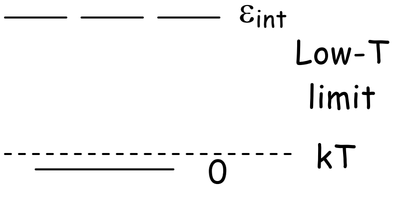
$$C_{V_{conf}} = \left(\frac{\partial U_{conf}}{\partial T}\right)_{V,N} = -\frac{1}{kT^2}\left(\frac{\partial U_{conf}}{\partial \beta}\right)_{V,N} = -\frac{N}{kT^2}\frac{\partial}{\partial \beta}\left(\frac{3\varepsilon_{\text{int}}e^{-\beta\varepsilon_{\text{int}}}}{1+3e^{-\beta\varepsilon_{\text{int}}}}\right)$$

$$= -\frac{3\varepsilon_{\text{int}}N}{kT^2}\frac{\left(1+3e^{-\beta\varepsilon_{\text{int}}}\right)\left(-\varepsilon_{\text{int}}e^{-\beta\varepsilon_{\text{int}}}\right) - e^{-\beta\varepsilon_{\text{int}}}\left(-3\varepsilon_{\text{int}}e^{-\beta\varepsilon_{\text{int}}}\right)}{\left(1+3e^{-\beta\varepsilon_{\text{int}}}\right)^2}$$

The function is complicated, but its limits are understandable. Also, it scales with N, so we can think of a configurational heat capacity per molecule.

$$C_{V_{conf}} \to 0 \text{ as } T \to 0$$

In the low-T limit, all the molecules are in the lowest state. If kT increases infinitesimally, all the molecules are still in the lowest state! So the configurational energy doesn't change!



$$C_{V_{conf}} \to 0 \text{ as } T \to \infty$$

In the high-T limit, the molecules are equally distributed among all the states. If kT increases, they are still equally distributed among all the states! So U_{conf} doesn't change.