5.60 Thermodynamics & Kinetics
Spring 2008

STATISTICAL THERMODYNAMICS

Calculation of macroscopic thermodynamic results

Entropically driven examples:

Free expansion of a gas

| V_1 gas | vacuum | $\longrightarrow$ | V_2 gas |
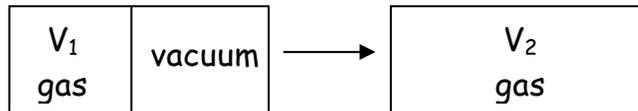
Lattice model for ideal gas translation:
Molecular volume v, Total volume V
All molecular positions have equal energy ε_{trans} = 0
All system microstates have equal energy E_{trans} = 0

Calculate $S = k\ln\Omega$ in each state

Molecular degeneracy g = V/v

System degeneracy Ω = g^N/N! = $(V/v)^N$/N!

For expansion from volume V_1 to V_2,

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

$$\Delta S = Nk\ln\frac{V_2}{V_1} = nR\ln\frac{V_2}{V_1}$$

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

N_A	N_B
V_A	V_B

$\longrightarrow$

$N = N_A + N_B$
$V = V_A + V_B$
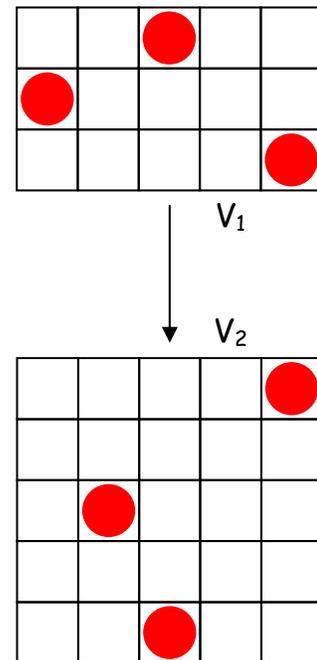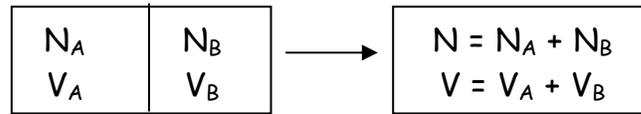
Assume same initial (p,T) for A & B $\Rightarrow$ same (p,T) for mixture
Assume equal molecular volumes & lattice cell sizes.
Then initially

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

After mixing: Count 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, divide by $N_A!N_B!$

So the final state entropy is

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

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

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

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

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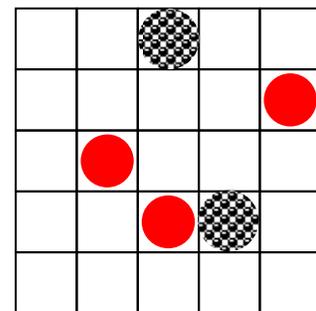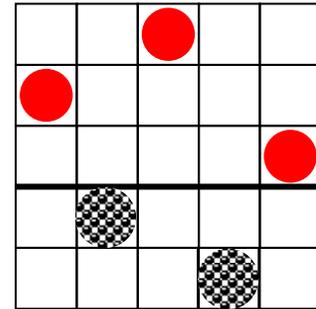
Ideal liquid mixture

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

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

$$S_B = k\ln\Omega_B = k\ln 1 = 0$$
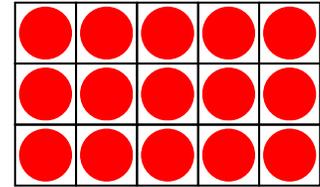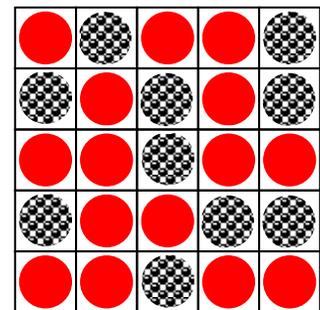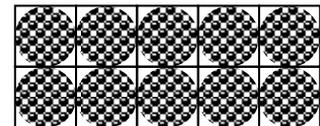
Mixture: N molecules for N sites.
First molecule has N choices, second (N – 1), etc.
ways to put the molecules into sites = N!
Correct for overcounting by dividing by $N_A!N_B!$

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

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

$$\Delta S_{mix} = Nk\ln N - \cancel{Nk} - (N_A k\ln N_A - \cancel{N_A k} + N_B k\ln N_B - \cancel{N_B k})$$

$$= (N_A + N_B)k\ln N - N_A k\ln N_A - N_B k\ln N_B = N_A k\ln\frac{N}{N_A} + N_B k\ln\frac{N}{N_B}$$

$$= -Nk(X_A \ln X_A + X_B \ln X_B)$$

Real liquid has additional states - positional disorder, molecular rotation, etc. – 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.
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Combinatorics:
Simple example
Mix 2 molecules A
+ 3 molecules B
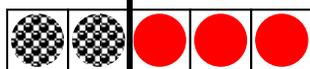
How many distinct
configurations Ω?
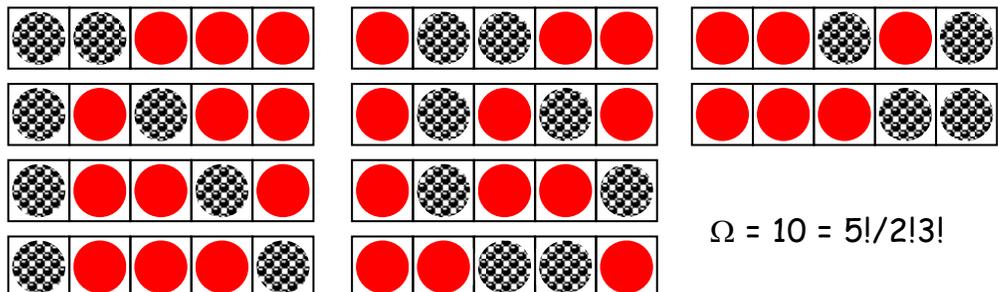
$\Omega = 10 = 5!/2!3!$

Energy & entropy changes
We saw one example earlier, with 4-segment polymers.

Molecular state:

Energy ε: 0 ε_{int} ε_{int} ε_{int}

Degeneracy g: 1   3
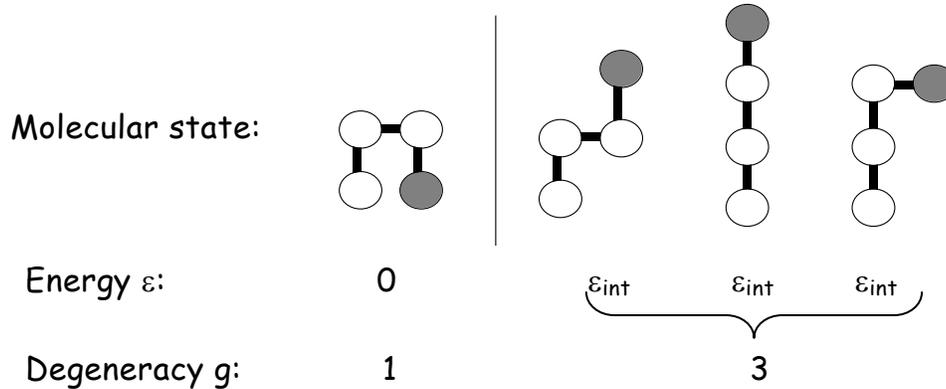
We've redefined the zero of energy as the ground state energy. "Configurational" molecular partition function is

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

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

For a solution of noninteracting polymer molecules,

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

We can determine the thermodynamic properties:

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

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

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

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

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

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

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

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

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

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

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

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

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

Scales with N, so we can think of a configurational heat capacity per molecule.

Complicated function, but its limits are understandable:

$C_{V_{conf}} \rightarrow 0$ as $T \rightarrow 0$

—— —— —— ε_{int}
                              Low-T
                              limit
- -
       ———— 0   kT

At low T, all molecules are in the lowest state. If kT increases infinitesimally, all the molecules are still in the lowest state! So the configurational energy U_{conf} doesn't change!

$C_{V_{conf}} \rightarrow 0$ as $T \rightarrow \infty$

- kT
                              High-T
                              limit
—— —— —— ε_{int}
       ———— 0
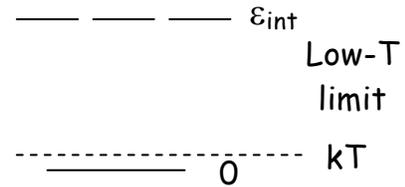
At high T, the molecules are equally distributed among all the states. If kT increases, they are still equally distributed among all the states! So U_{conf} doesn't change.
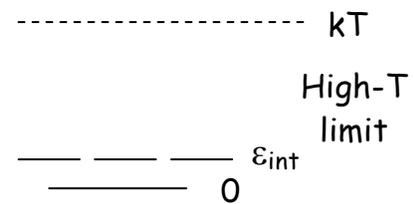
The low-T limit $C_V \rightarrow 0$ is common to almost every degree of freedom since ultimately a temperature is reached at which only the lowest level is occupied.

The high-T limit $C_V \rightarrow 0$ is characteristic of systems or degrees of freedom with a finite number of states, i.e. a maximum possible energy. In that case, ultimately a temperature is reached at which the equilibrium distribution is ~ equal probability of all the levels being occupied. This is the case for molecular configurations as discussed here and for spin states of nuclei and electrons.