Chapter 7 (the skinny)

Example of a partition function:

Consider an ideal gas in a cube of side L.

$$Z(L,T) = \sum_j e^{-E_j/kT}$$

$$= C \int_0^L d^3r_1 \cdots d^3r_N \int_{-\infty}^{\infty} d^3p_1 \cdots d^3p_N \, e^{-\frac{\sum \vec{p}_i^{\,2}/2m}{kT}} \qquad (7.1)$$

in which C contains constant factors like the internal energies ϵ_i of the molecules. By p. 224,

$$F = -kT \ln Z$$

$$= -kT \ln C L^{3N} D$$

$$= -NkT \ln L^3 + \text{constant}.$$

The pressure p is

$$p = -\frac{dF}{d(L^3)} = \frac{NkT}{L^3} = \frac{NkT}{V} \qquad (7.2)$$

which is the ideal-gas law.

Fixed-pressure approach:

$$P(r_1 \cdots p_N, L, p) = C_1 \exp\left[-\left(\frac{\sum \vec{p}_i^{\,2}}{2m} + \frac{\vec{P}^{\,2}}{2M} + fL\right)/kT\right] \tag{7.3}$$

$$\langle L\rangle = \frac{\int L\ P(r_1 \cdots p_N L, p)\, d^3r_1 \cdots d^3p_N\, d^3p\, dL}{\int P(r_1 \cdots p_N, L, p)\, d^3r_1 \cdots d^3p_N\, d^3p\, dL} \tag{7.4}$$

$$= \frac{\int_0^\infty dL\ e^{-fL/kT} L^{N+1}}{\int_0^\infty dL\ e^{-fL/kT} L^N} \tag{7.5}$$

7A (a) Integrate by parts: $[fg]_a^b = \int dx\, f'g + \int dx\, fg'$.

$$\langle L\rangle = \frac{\int_0^\infty dL\,(N+1)L^N e^{-fL/kT}/(f/kT)}{\int_0^\infty dL\, L^N e^{-fL/kT}} = (N+1)\frac{kT}{f}.$$

(b) Let $N+1 \approx N$, then $\langle L\rangle f = NkT$, $f = pA$,

So $LpA = NkT = pV = NkT$. Also

$$\langle L\rangle = -kT\frac{d}{df}\ln\int C_1 e^{-(\frac{1}{2m}\sum p_i^2 + \frac{1}{2M}P^2 + fL)/kT} d^3r_1 \cdots d^3p_N\, d^3p\, dL = -kT\frac{d}{df}\ln Z(f).$$

$L = \frac{V}{A}$, $f = pA$, so $V = -kT\, d\ln Z(p)/dp = dF(p)/dp$.

Osmotic Pressure

We may think of a dilute solution of a solute in a solvent as two mixed ideal gases. The pressure p then is

$$pV = (N_1 + N_2) kT$$

where N_1 is the number of solute molecules, e.g. sugar, and N_2 is the number of solvent molecules, e.g., water.

If N_1 is zero on one side of a <u>semipermeable</u> membrane that stops solute molecules but lets solvent molecules pass, then across the membrane

$$\Delta p = \frac{N_1}{V} kT = c_1 kT, \qquad (7.7)$$

which is the van't Hoff relation.

7B $$W = \int F\,dL = \int pA\,dL$$

$$= \int p\,dV = \int ckT\,dV$$

$$= kT \int \frac{N_1}{V}\,dV = N_1 kT \ln \frac{V_2}{V_1}.$$

If $V_2 = 2V_1$, then with $kT_r = 4.1 \times 10^{-21}$ J,

$$W = N_1 kT_r \ln 2 = 2.8 \times 10^{-21}\ \text{J} \times N_1.$$

So the γ of Eq. (1.7) is $\gamma = \ln 2 = 0.69$.

How big is the osmotic pressure due to the various molecules in a cell? Globular proteins are blobs ≈ 20 nm wide and make up 30% of the volume of a red blood cell stuffed with hemoglobin. So the <u>volume fraction</u> ϕ is

$$\phi = 0.3 = \frac{N}{V}\,\frac{4}{3}\pi r^3 = c\,\frac{4}{3}\pi \left(10^{-8}\text{m}\right)^3 \qquad (7.8)$$

so $$c \approx 7 \times 10^{22}\ \text{m}^{-3}.$$

Nelson sets $M \equiv \frac{\text{mole}}{L} = \frac{6\,10^{23}}{10^{-3}\,m^3} = 6\,10^{26}\,m^{-3}$.

So the proteins in a red blood cell are a

$$\frac{c}{M}M = \frac{7\,10^{22}}{6\,10^{20}} = 1.2 \times 10^{-4}\,M \text{ solution}$$

That's a 0.12 mM solution.

In water, the pressure trying to burst the cell is

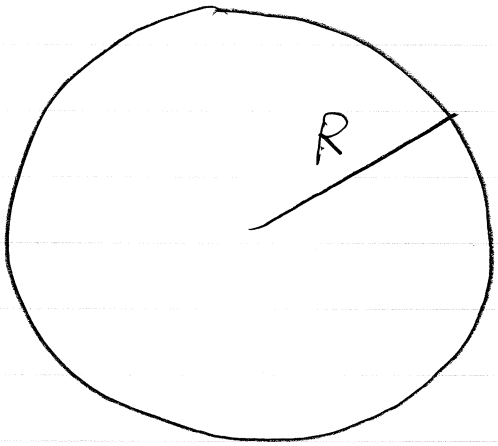
$$p = chT = 7\times10^{22}\,m^{-3}\,4.1\times10^{-21}\,J$$

$$p \approx 300\,Pa$$

which is small compared to atmospheric pressure, 10^5 Pa. Is this big for a cell?

Surface tension Σ is force per unit length or energy per unit area

$$[\Sigma] = \frac{F}{L} = \frac{FL}{L^2} = \frac{E}{A}.$$



$$p\,dV = p\frac{dV}{dR}dR = p4\pi R^2 dR = \Sigma\, dA = \Sigma\, 8\pi R\, dR$$

So

$$\Sigma = \frac{pR}{2} \qquad (7.9)$$

which is Laplace's formula. For a cell with $R = 10\,\mu m = 10^{-5}\,m$ and $p = 300\,Pa$, Σ is

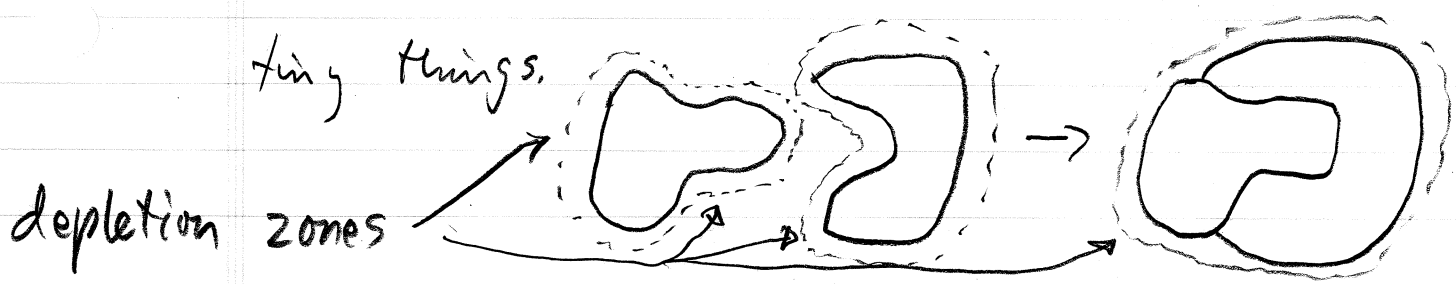
$$\Sigma = \frac{300\,Pa\,10^{-5}\,m}{2}$$

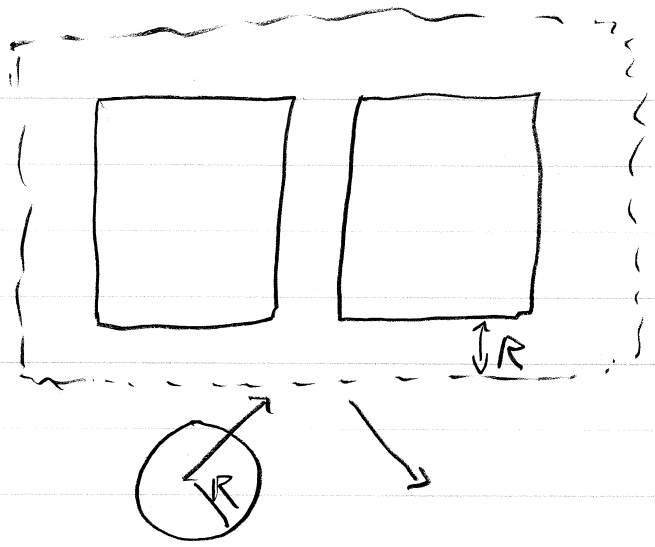
$$= 1.5 \times 10^{-3}\,N\,m^{-1}$$

which is enough to rupture the cell membranes of some eukaryotic cells.

Salt is worse. A 1M solution of salt has 10^{27} ions per m^3. So red blood cells burst or lyse in pure water.

The depletion interaction or molecular crowding. In 1954, Asakura & Oosawa noticed that large things, when surrounded by many small things of radius R, are surrounded by a depletion zone of thickness R because the small things cannot get closer than R. If the big things fit together snugly, then parts of their two depletion zones vanish, which means more space for the tiny things.





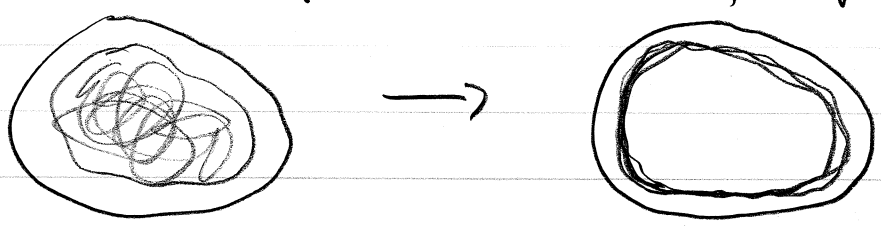
It's as if there were a semipermeable membrane wrapped around the big things at a distance R. The pressure drop is

$$p = c k T$$

so if we bring the blocks of area A together, the change in the free energy is

$$\Delta F = p \Delta V = c k T A 2R . \qquad (7.10)$$

Look at Fig. 7.4: when tiny things are added



Coiled polymers and/or globular proteins can help big molecules fit together. Both bovine serum albumin (BSA) and polyethylene glycol (PEG, a polymer) reduce the solubility of deoxyhemoglobin by as much as a factor of 10. Dextran &/or PEG can increase the melting point of DNA by several degrees and make protein complexes 10 times more stable. E. Coli's DNA polymerase needs some crowding agent to work properly. The insides of cells, of course, are crowded.

Think of fluid in which a force $F(z)$ pushes in the z direction. Let $p(z)$ be the pressure at z.

In equilibrium (7.12)

$$\left[-p\left(z+\tfrac{1}{2}dz\right)+p\left(z-\tfrac{1}{2}dz\right)\right]dxdy+F(z)\,dxdydz=0$$

so $\dfrac{dp}{dz}=F(z)$ in <u>hydrostatic equilibrium.</u>

If $F=-\rho g$, then $\dfrac{dp}{dz}=-\rho g$ or

$$p(z)=p_0+\rho g(z_0-z). \qquad (7.11)$$

At low Reynolds numbers, $F(z)=c(z)f(z)$

$$\frac{dp}{dz}=c(z)f(z)=c(z)\left(-\frac{dU(z)}{dz}\right). \qquad (7.13)$$

Assume $U\to 0$ far from wall / membrane.

Boltzmann said $c(z)=c_0 e^{-U(z)/kT}$, so

$$\frac{dp}{dz}=-c_0 e^{-U(z)/kT}\frac{dU(z)}{dz}=kT\frac{dc(z)}{dz}$$

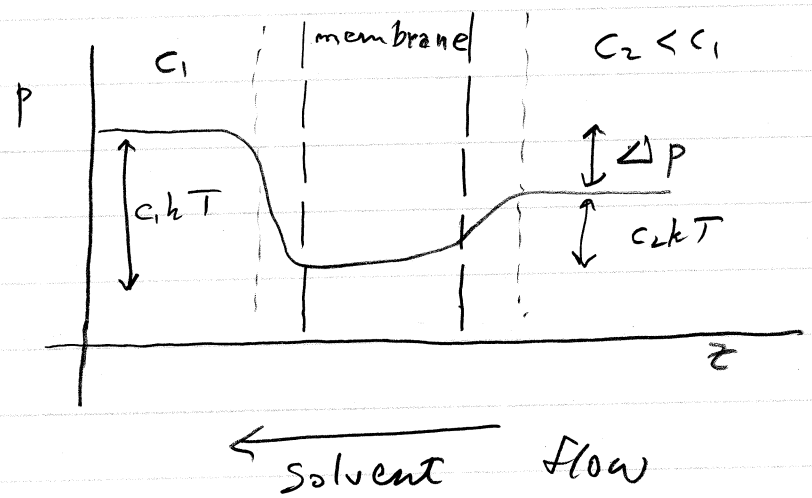
which implies

$$\Delta p=kT\,\Delta c. \qquad (7.14)$$

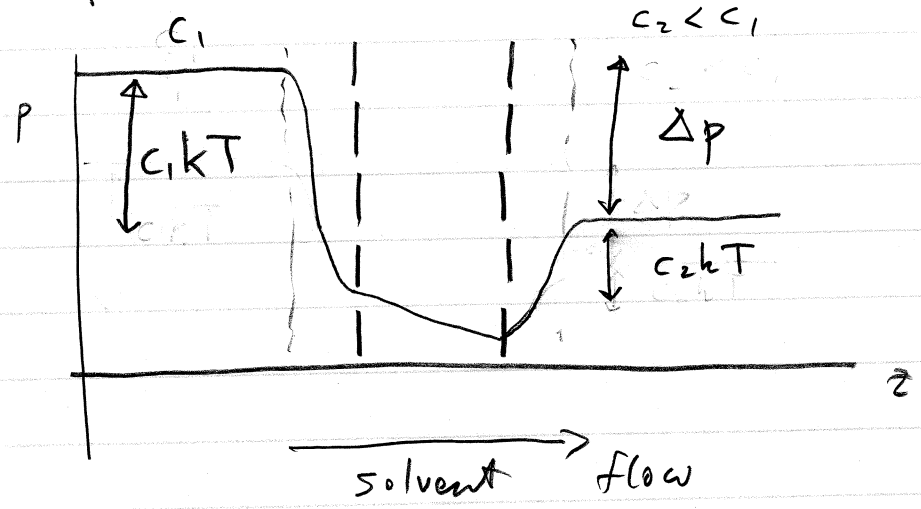
7C $\qquad \Delta p = kT\Delta c$

We take $\Delta p = p_1 - p_2 > 0$ and $\Delta c = c_1 - c_2 > 0$.

If $\Delta p < kT\Delta c$, then



But if $\Delta p > kT\Delta c$, then



To stop flow, i.e., to have equilibrium, we need $\Delta p = kT\Delta c$.

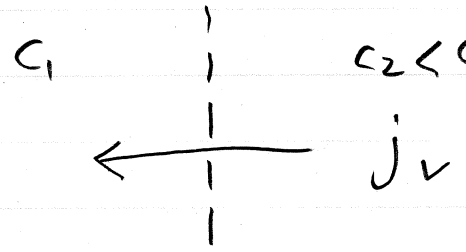
Suppose $\Delta p \neq kT\Delta c$. Then the solvent will flow thru the semipermeable membrane with a volume flux j_v given by

$$j_v = -L_p(\Delta p - kT\Delta c). \qquad (7.15)$$

where L_p is a constant called the <u>filtration coefficient.</u>

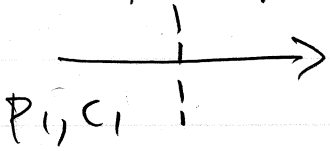
Thus if $\Delta p = 0$, then

$$j_v = L_p kT \Delta c.$$



But if $\Delta p = p_1 - p_2 > 0$ and $\Delta p > kT\Delta c$, then

$$j_v = -L_p(\Delta p - kT\Delta c)$$



Electrostatics and the Poisson-Boltzmann Eq.

Electrostatic potential energy of a shell of charge q and radius R is

$$U = \frac{1}{2} q V(R)$$

where

$$V(R) = \frac{q}{4\pi\varepsilon_0 R} .$$

So

$$U = \frac{q^2}{8\pi\varepsilon_0 R} .$$

Here $\frac{e^2}{4\pi\varepsilon_0} = 2,3 \cdot 10^{-28}$ Jm

where e is the charge of the electron.

For instance, the work required to remove an electron from 1% of the water molecules in a drop of radius $R = 1$ mm is $2 \cdot 10^{-11}$ J!

This energy is proportional to R^5,

so for a drop of $R = 1\,\mu m$, the work would be $W = U = 2 \cdot 10^{-4}\,J$, still much more than kT.

If the drop were in water, we would replace ϵ_0 by $\epsilon = 80\epsilon_0$.

So the work needed to remove an electron from 1% of the H_2O molecules of a droplet of $R = 1\,\mu m$ in water is

$$\frac{q^2}{8\pi\epsilon R} = 2.7 \times 10^{-6}\,J$$

which still is big compared to kT.

For $R = 1\,nm$, the work $W = U$ shrinks by a factor of $(10^{-3})^5 = 10^{-15}$ and now is $W = 2.7 \times 10^{-21}\,J \approx 0.7\,kT_r$ where T_r is room temperature.

The lesson is that bulk matter is electrically neutral, but charged matter can occur on the nm scale.

DNA ⇒ a <u>macroion</u>. It's PO_4^- groups give it a negative charge. It is surrounded in solution by a cloud of positive <u>counterions</u>, which being positive are called <u>cations</u>. The negative DNA macroion is an <u>anion</u>.

In vacuum and in dielectrics, electric fields often fall off slowly with distance as $\frac{1}{r^2}$ or $\frac{1}{r^3}$. But in saline solutions, the ions shield charges, and fields are screened at ≈ 1 nm.