Redo the midterm exam and hand it in. (10 points)
It is posted on the web. Just download a clean copy and hand it in with this problem set.
To get the most out of this, I suggest:

- Take a quiet moment when you have some time and go over your exam carefully.
- For the problems or parts of problems that you did not get right, see if you can figure out what went wrong before looking at the solutions on line.
- Look on line for things that still confuse you. If you do not understand, talk with friends or ask me.
- When you have sorted through the exam in this way, then sit down with the blank exam and see how far you can get without resorting to aids but not under time pressure.
- Finish up by filling in what you could not get done this way by using available aids.

Note: If you just copy my solutions or someone else's, this will not be a useful exercise. Once you have sorted out the roadblocks, put the solutions in your own words. That's important.

16. Approach to equilibrium of $A + B \leftrightarrow C$. (continued from Lect. 21)
I showed you in class that in a spatially uniform environment the equations of motion governing approach to equilibrium are:

$$\frac{dn_C}{dt} = -k_- n_C + k_+ (m_A - n_C)(m_B - n_C) = -\frac{dn_A}{dt} = -\frac{dn_B}{dt},$$

along with "conservation laws" stating that

$$\begin{cases} m_A \equiv n_A^0 + n_C^0 = n_A(t) + n_C(t) \\ m_B \equiv n_B^0 + n_C^0 = n_B(t) + n_C(t) \end{cases}$$

are time independent.

(a) (1 point) Show that $0 \le n_C \le \min(m_A, m_B)$ for any time t.

(a) This results follows from $\begin{cases} m_A = n_A + n_C \\ m_B = n_B + n_C \end{cases}$, with m_A, m_B, n_A, n_B, and n_C all non-negative.

(b) (4 points) When the system comes to equilibrium, what are the final concentrations n_α^f in terms of the initial concentrations?
Hints:
You will find a quadratic equation for n_C^f with two (real) solutions n_+ and n_-. One of them violates the condition (a), so you will be able to choose the physical one.

(b) The equation for the equilibrium concentration is

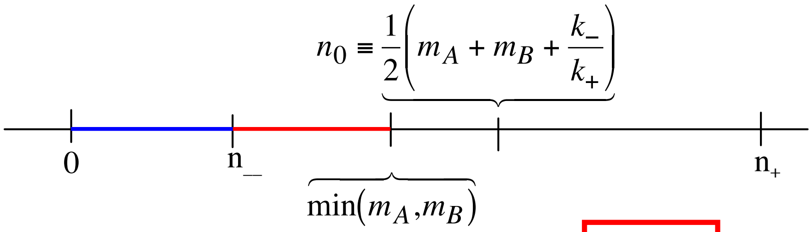
$$\begin{aligned} &(n_C - m_A)(n_C - m_B) - \frac{k_-}{k_+} n_C = 0 \\ &n_C^2 - \left(m_A + m_B + \frac{k_-}{k_+} \right) n_C + m_A m_B = 0 \end{aligned},$$

so $n_C = n_\pm = \frac{1}{2}\left[\left(m_A + m_B + \frac{k_-}{k_+} \right) \pm \sqrt{\left(m_A + m_B + \frac{k_-}{k_+} \right)^2 - 4 m_A m_B} \right]$.

Note that

$$0 \le \left(m_A + m_B + \frac{k_-}{k_+} \right)^2 - 4 m_A m_B \le \left(m_A + m_B + \frac{k_-}{k_+} \right)^2 \text{ and } 0 \le \min(m_A + m_B) \le \frac{1}{2}\left(m_A + m_B + \frac{k_-}{k_+} \right).$$

It follows from these inequalities that the structure of the roots is as shown below:



Thus, the n_+ root violates the condition (a), so we conclude $\boxed{n_C^f = n_-.}$

The original equation can now be written $\frac{dn_C}{dt} = k_+(n_C - n_+)(n_C - n_-)$.

(c) (5 points) Now, integrate the differential equation for $n_c(t)$ subject to the initial condition $n_C(t=0) \equiv n_C^0$.

Hint: Integration will give you logarithms, which you must treat carefully, so that you don't end up with logarithms of negative quantities. For this reason, I advise doing separately the two cases $n_C^0 < n_C^f$ and $n_C^0 > n_C^f$.

(c) The physically-meaningful region for $n_C(t)$ is the colored part of the axis.

Note that the sign of the of the right side of the equation for $\frac{dn_C}{dt}$ (above) is positive in the blue region (so points in the blue region flow to the right towards n_-) but negative in the red region (so points in the red region flow to the left towards n_-), showing that n_C^f is an "attractor" for the entire physical region.

The differential equation can now be written $\frac{dn_C}{(n_C - n_+)(n_C - n_-)} = k_+ dt$

or $\left[\frac{1}{n_C - n_+} - \frac{1}{n_C - n_-}\right] dn_C = k_+(n_+ - n_-)dt$.

It is at this point that you have to be careful about signs. I will do the blue region and leave the red region to you:

In the blue region, $n_- > n_C$ and $n_+ > n_C$, so I rewrite the equation to make the denominators positive,

$\left[-\frac{1}{n_+ - n_C} + \frac{1}{n_- - n_C}\right] dn_C = k_+(n_+ - n_-)dt$ which integrates to $\ln\left(\frac{n_+ - n_C}{n_- - n_C}\right) = k_+(n_+ - n_-)t + \text{const.}$ or

$\left(\frac{n_+ - n_C}{n_- - n_C}\right) = \frac{1}{A} e^{k_+(n_+ - n_-)t}$, which can be solved for $n_C(t)$ $\boxed{n_C(t) = n_-\left[\frac{1 - A\frac{n_+}{n_-}e^{-k_+(n_+ - n_-)t}}{1 - Ae^{-k_+(n_+ - n_-)t}}\right]}$,

which approaches $n_- = n_C^f$ as $t \to \infty$. It remains to fit the initial condition,

$n_C(0) = n_C^0 = n_-\left[\frac{1 - A\frac{n_+}{n_-}}{1 - A}\right]$, so $A = \frac{n_- - n_C^0}{n_+ - n_C^0}$ (which shows that 0<A<1).

The final result for the red region is $\boxed{n_C(t) = n_-\left[\frac{1 + B\frac{n_+}{n_-}e^{-k_+(n_+ - n_-)t}}{1 + Be^{-k_+(n_+ - n_-)t}}\right]}$ with $B = \frac{n_C^0 - n_-}{n_+ - n_C^0}$ (0<B<1).

(d) (2 points) Show that in both cases the final approach to equilibrium is exponential with $e^{-t/\tau}$. What is the timescale τ? Note that t depends on the initial concentrations of the reacting species. Why is this reasonable to expect?

(d) Approaching equilibrium, the exponential terms are small and can be expanded, so for the blue region, $n_C(t) = n_-\left[\frac{1-A\frac{n_+}{n_-}e^{-k_+(n_+-n_-)t}}{1-Ae^{-k_+(n_+-n_-)t}}\right] \xrightarrow[t\to\infty]{} n_-\left[1-A\left(\frac{n_+-n_-}{n_-}\right)e^{-k_+(n_+-n_-)t}+\text{small}\right]$.

The timescale is $\frac{1}{\tau} = k_+(n_+-n_-) = k_+\sqrt{\left(m_A+m_B+\frac{k_-}{k_+}\right)^2-4m_Am_B}$

The same exponent arises for the red region.
The initial concentrations are encoded in m_A and m_B. You can see that if these quantities are large, then 1/τ is large, i.e., τ is small. This is reasonable since high particle densities mean that the reaction proceed faster.

17. Polymerization reactions (after PKT problem 6.6).
In polymerization of a monomer X to form successively longer chains XX=X_2, XXX=X_3, …, each added monomer sees the same environment, so all the equilibrium constants are the same, i.e., $X + X_n \overset{K}{\leftrightarrow} X_{n+1}$, with the same K for all n.

(a) (2 points) Suppose you know the *equilibrium* concentration of the monomer $x \equiv [X] = [X_1]$. Show that the equilibrium concentration of the n-mer is $[X_n] = K^{n-1}x^n$. n is called the "degree of polymerization."

(a) This is just an recursive calculation:

$$[X_1] = x$$

$$[X_2] = K[X_1]^2 = x(Kx)$$

$$[X_3] = K[X_1][X_2] = x(Kx)^2$$

…

$$[X_n] = K[X_1][X_{n-1}] = \boxed{x(Kx)^{n-1}}$$

(b) (2 points) Suppose you pick a polymer (any n-mer, n=1,2,…) at random out of the solution. Show that the probability P_n that it will be an n-mer is $P_n = \frac{(Kx)^{n-1}}{Q}$, where $Q = 1 + Kx + (Kx)^2 + \ldots = \frac{1}{1-Kx}$ is called the "binding polynomial."

(b) The probability of finding an n-mer is $P_n = \frac{[X_n]}{[X_1]+[X_2]+[X_3]+\ldots} = \frac{x(Kx)^{n-1}}{x\left[1+(Kx)+(Kx)^2+\ldots\right]} = \boxed{\frac{(Kx)^{n-1}}{Q} = (Kx)^{n-1}(1-Kx)}$.

Note that in summing the geometric series, I am assuming Kx<1. We'll see in (e) that this is always the case.

(c) (2 points) Show that the mean degree of polymerization is $\langle n\rangle = \frac{d}{d(Kx)}\ln Q = \frac{1}{1-Kx}$.

(c) We are picking a *polymer* at random out of the solution and noting its degree of polymerization n. Thus,

$$\langle n\rangle=\sum_{n=1}^{\infty}nP_n=(1-Kx)\sum_{n=1}^{\infty}n(Kx)^{n-1}=(1-Kx)\frac{dQ}{d(Kx)}=\frac{1}{Q}\frac{dQ}{d(Kx)}=\frac{d\ln Q}{d(Kx)}=\frac{d}{d(Kx)}\left(\ln\left(\frac{1}{1-Kx}\right)\right)\boxed{=\frac{1}{1-Kx}}.$$

(d) (2 points) Suppose that the polymer mixture was prepared initially by somehow putting into the solution an initial concentration x_0 of monomers (only). Show that $x_0=\frac{x}{(1-Kx)^2}$.

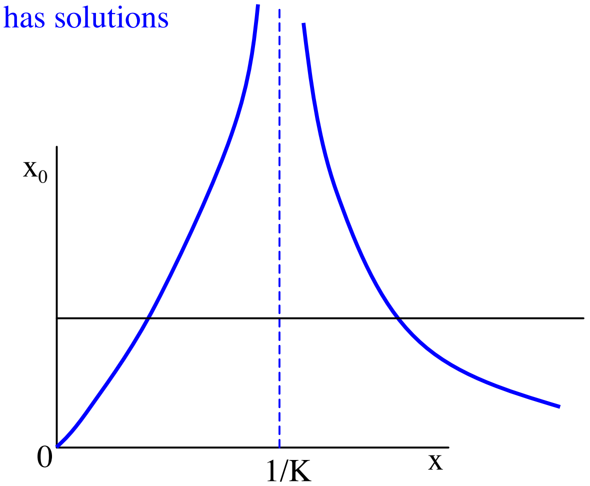
(d) The total concentration of monomers in the equilibrium solution is

$$x_0=\sum_{n=1}^{\infty}n[X_n]=\sum_{n=1}^{\infty}nx(Kx)^{n-1}=x\sum_{n=1}^{\infty}n(Kx)^{n-1}=\frac{x\langle n\rangle}{(1-Kx)}\boxed{=\frac{x}{(1-Kx)^2}},$$ where I used the result of (c).

(e) (2 points) Now, turn this around and solve for x as a function of x_0, so that you can see how x depends on the gross monomer concentration.
Hint: You will find two solutions of the quadratic equation. Which is the physical one?

(e) The quadratic is $K^2x_0x^2-(2Kx_0+1)x-x_0=0$, which has solutions

$$x=\frac{(2Kx_0+1)\pm\sqrt{4Kx_0+1}}{2K^2x_0}.$$



It is easiest to see what is going on graphically:
The physical branch of solutions is the one at the left for which $x \sim x_0$ at small x. Indeed, conservation of particles requires $x \le x_0$, which is violated by the right hand branch, so

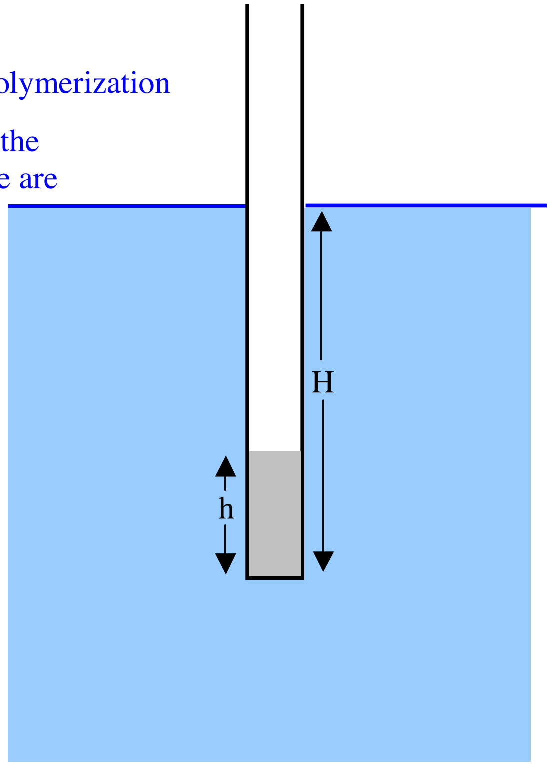
$$\boxed{x=\frac{(2Kx_0+1)-\sqrt{4Kx_0+1}}{2K^2x_0}.}$$

Note that for the physical branch, $0 \le Kx < 1$ for any x_0.

(f) (2 points) What is the limit of Kx as x_0 gets large? What does this mean about the mean degree of polymerization?

(f) As x_0 increases, Kx approaches 1 from below.
We found in (c) that $\langle n\rangle=\frac{1}{1-Kx}$, so the mean degree of polymerization increases without limit. Indeed, you can see from (b) that the probability P_n becomes very flat as a function of n, so there are more and more very-long polymers in the distribution.

18. Reverse osmosis, desalination.
Seawater is a salt solution of roughly 1M in concentration.
A long pipe is inserted into the sea, as shown at the right.
It is open at the top but closed at the bottom by a semipermeable membrane which passes water but not salt.
If the pipe is inserted to a sufficient depth H, fresh water accumulates in the bottom, as shown in the figure.
(a) (6 points) What is the minimum depth H_{min} at which fresh water will appear?



(a)

Comment: I gave this problem on the final exam when I last taught Phys. 347.

Water will begin to flow through the semipermeable membrane when the gravitational pressure difference, $\Delta P_{grav} = \rho g H_{\min}$, exceeds the osmotic pressure difference $\Delta P_{osm} = \Delta c_s k_B T$, which is 22.4 atmospheres at standard temperature and pressure, as I mentioned at Lect. 20.3 (1 atm=1.01x10^5 N/m^2). Thus, $H_{\min} = \frac{22.4\left(1.01\times 10^5\right)}{10^3(9.8)} = \boxed{231\,m\,.}$

Note: If you assumed a warmer temperature than 0 C you will get a correspondingly higher osmotic pressure and a correspondingly larger H_{min}. Thus, it you take water at 300 C, you will find

$$H_{\min} = 231\cdot\frac{300}{273} = 254\ m.$$

(b) (2 points) For H>H_{min} what will be the equlibrium height h of the fresh water in the pipe?

Note:

Ignore the difference in density between fresh water and seawater.

Comment: This is actually an appreciable correction. Salt water is appreciably denser than fresh. Indeed, water does not expand much when you add a mole/litre of salt (try it in a water glass!). Thus adding 1 mol of NaCl increases its mass by 11+17= 28 grams for 1000 g water, an increase of almost 3%.

(b) This question is worded in a slightly misleading way. Actually, what happens for depths greater than H_{min} is that the difference between H and h remains fixed at H_{min}. The reason is not hard to see: The pressure difference across the membrane remains at $\Delta P_{osm} = \Delta c_s k_B T$; however, now the gravitational pressure difference is ρg(H-h).

19. Problem:

In a water-filled container of volume V at temperature T, we introduce N_0 identical solute particles A. These particles can combine to form dimers following the reaction $2A \leftrightarrow A_2$. Thus, at equilibrium the number N_A^f of remaining uncombined A particles is less than N_0, the difference having been combined into dimers. The law of mass action requires $\frac{n_{A_2}}{n_A^2} = K_{eq}(T)$.

(a) (2 points) What is the relation between the chemical potentials the species of A and A_2 at equilibrium?

(b) (3 points) What is the formula for the equilibrium constant $K_{eq}(T)$?

(c) (3 points) In terms of N_0 and K_{eq}, what is the final number N_A^f of uncombined A's?

Note: You can do (a) and (c) without doing (b).

This, also, is from an old exam—slightly modified.

(a) The reaction is $2A \leftrightarrow A_2$, so the relation is $\boxed{2\mu_A = \mu_{A_2}}$.

(b) All that is needed is the expression for the chemical potentials in terms of the particle densities. From your midterm formula sheet,

$n = \frac{z(T)e^{-\varepsilon_s/k_BT}\cdot e^{\mu/k_BT}}{\lambda_{th}^3}$, so $e^{\mu_A/k_BT} = \frac{n_A\lambda_{th,A}^3 e^{\varepsilon_{s,A}/k_BT}}{z_A(T)}$ and similarly for A_2. It follows that

$$e^{2\mu_A/k_BT} = \left(\frac{n_A\lambda_{th,A}^3 e^{\varepsilon_{s,A}/k_BT}}{z_A(T)}\right)^2 = \frac{n_{A_2}\lambda_{th,A_2}^3 e^{\varepsilon_{s,A_2}/k_BT}}{z_{A_2}(T)} = e^{2\mu_{A2}/k_BT}.$$

Thus, $\boxed{\frac{n_{A_2}}{n_A^2} \equiv K_{eq} = \frac{\lambda^6_{th,A}}{\lambda^3_{th,A_2}} \cdot \frac{z_{A_2}(T)}{\left(z_A(T)\right)^2} \cdot e^{\left(2\varepsilon_{s,A}-\varepsilon_{s,A_2}\right)/k_BT}}$.

Comment:
The three factors which make up the equilibrium constant are the ratios of thermal wavelengths, internal partition functions, and solvation-energy weights. For many circumstances, the most important factor is the internal partition functions, which carry the leading factor $\frac{e^{-\beta E^0_{A_2}}}{e^{-2\beta E^0_A}} = e^{\frac{B}{k_BT}}$, where $B = 2E^0_A - E^0_{A_2} > 0$ is the amount by which the ground-state energy of 2A is higher than the ground-state energy of the bound A_2. When B is large, the equilibrium is push strongly to the right.

(c) The equations which determine the final concentrations are $n_0 = n_A + 2n_{A_2}$, which expresses conservation of the total number of A particles (free and combined) and $\frac{n_{A_2}}{n_A^2} = K_{eq}$, which expresses the law of mass action. Substitution leads to a quadratic equation for n_A, the solution of which gives, $n_A = \frac{1}{2K_{eq}}\left[-\frac{1}{2} \pm \sqrt{\frac{1}{4} + 2Kn_0}\right]$. We can discard the "-" root, which is negative (unphysical), so the final solution is $\boxed{N_A^f = \frac{V}{2K_{eq}}\left[-\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{2KN_0}{V}}\right]}$.

20. Complex receptor

Consider a receptor (immersed in aqueous solution of ligands L) which has two internal states, A and B, with energies $\varepsilon_A > \varepsilon_B > 0$, so that at fixed temperature T the state A is less likely than the state B. The receptor can bind (or not bind) a ligand L in either state A or state B. When the binding occurs in state A, the binding energy is ε_{AL}, and when the binding occurs in state B, the binding energy is ε_{BL}, with $0 > \varepsilon_{BL} > \varepsilon_{AL}$, so that the binding process is more favorable in state A, even though the unbound A is more energetic than the unbound B. Note that there are overall four possible states of the receptor A0 (empty), B0, AL and BL.
You are going to do this problem in the grand canonical representation (Lect. 21).
You are going to represent this system in terms of two 2-state variables, $\sigma = 0,1$ with $\sigma=0$ giving the A state and $\sigma=1$ giving the B state, and $\tau = 0,1$, with $\tau=0$ giving the empty state and $\tau=1$ giving the ligand-bound state.

(a) (5 points) Show that the quantity $\left(E_n - \mu_L N_n\right)$ (μ_L is the ligand chemical potential) can be represented in terms of σ and τ according to (correction)

$$\left(E_n - \mu_L N_n\right)_{\sigma,\tau} = \varepsilon_A + \left(\varepsilon_B - \varepsilon_A\right)\sigma + \left(\varepsilon_{AL} - \varepsilon_A - \mu_L\right)\tau + \left(\varepsilon_A - \varepsilon_B - \varepsilon_{AL} + \varepsilon_{BL}\right)\sigma\tau .$$

(b) (2 points) Show that:

- the probability of finding the receptor in state A (empty or full) is $P_A \equiv \langle 1 - \sigma \rangle$.
- the probability of finding the receptor in state B (empty or full) is $P_B \equiv \langle \sigma \rangle$.
- the probability of finding the receptor binding a ligand (either in A or in B) is $P_L \equiv \langle \tau \rangle$.

(c) (3 points) Calculate the probabilities P_A, P_B, and P_L in terms of the ligand density n_L.

Hint: Treat the ligands in solution as ideal, so $e^{\frac{\mu_L}{k_BT}} = n_L \lambda^3_{th,L} e^{\frac{\varepsilon_s}{k_BT}}$, as in Lect. 21.

Comment: The purpose of this problem is to give you a little experience of thinking in terms of the 2-state variables.

(a) An easy way to do this is in terms of what are technically called "projection operators" for the four states of the system i.e., quantities which have the value 1 in the designated state and 0 in all other states.

Thus,

state (n)	values (σ,τ)	projection	E_n-μN_n
A0	(0,0)	(1-σ)(1-τ)	ε_A
B0	(1,0)	σ(1−τ)	ε_B
AL	(0,1)	(1−σ)τ	$\varepsilon_A+\varepsilon_{AL}-\mu$
BL	(1,1)	στ	$\varepsilon_B+\varepsilon_{BL}-\mu$

Thus, $$\boxed{(E-\mu N)_{\sigma,\tau}=\varepsilon_A(1-\sigma)(1-\tau)+\varepsilon_B\sigma(1-\tau)+(\varepsilon_A+\varepsilon_{AL}-\mu_L)(1-\sigma)\tau+(\varepsilon_B+\varepsilon_{BL}-\mu_L)\sigma\tau.}$$

Multiplying this out gives the result quoted above.

Alternatively and equivalently, simply verify that the formula above gives the energies in the table.

(b) These results are direct, when you realize that:
(1-σ)=1 for states A and AL and zero otherwise,
σ=1 for state B and BL and zero otherwise, and
τ=1 for states AL and BL and zero otherwise.

(c) Calculating averages is direct:
First calculate the Grand partition function:

$$\Xi=\sum_n e^{-\beta(E_n-\mu_L N_n)}=\sum_{\sigma,\tau}e^{-\beta(E-\mu_L N)_{\sigma,\tau}}=e^{-\beta\varepsilon_A}+e^{-\beta\varepsilon_B}+e^{-\beta(\varepsilon_A+\varepsilon_{AL}-\mu_L)}+e^{-\beta(\varepsilon_B+\varepsilon_{BL}-\mu_L)}.$$

Then,

$$P_A=\frac{1}{\Xi}\sum_{\sigma,\tau}(1-\sigma)e^{-\beta(E-\mu N)_{\sigma,\tau}}=\frac{e^{-\beta\varepsilon_A}+e^{-\beta(\varepsilon_A+\varepsilon_{AL}-\mu_L)}}{e^{-\beta\varepsilon_A}+e^{-\beta\varepsilon_B}+e^{-\beta(\varepsilon_A+\varepsilon_{AL}-\mu_L)}+e^{-\beta(\varepsilon_B+\varepsilon_{BL}-\mu_L)}},$$

$$P_B=\frac{1}{\Xi}\sum_{\sigma,\tau}\sigma e^{-\beta(E-\mu N)_{\sigma,\tau}}=\frac{e^{-\beta\varepsilon_B}+e^{-\beta(\varepsilon_B+\varepsilon_{BL}-\mu_L)}}{e^{-\beta\varepsilon_A}+e^{-\beta\varepsilon_B}+e^{-\beta(\varepsilon_A+\varepsilon_{AL}-\mu_L)}+e^{-\beta(\varepsilon_B+\varepsilon_{BL}-\mu_L)}},\text{ and}$$

$$P_L=\frac{1}{\Xi}\sum_{\sigma,\tau}\tau e^{-\beta(E-\mu N)_{\sigma,\tau}}=\frac{e^{-\beta(\varepsilon_A+\varepsilon_{AL}-\mu_L)}+e^{-\beta(\varepsilon_B+\varepsilon_{BL}-\mu_L)}}{e^{-\beta\varepsilon_A}+e^{-\beta\varepsilon_B}+e^{-\beta(\varepsilon_A+\varepsilon_{AL}-\mu_L)}+e^{-\beta(\varepsilon_B+\varepsilon_{BL}-\mu_L)}}.$$

Substituting for $e^{\beta\mu_L}$ gives these probabilities in terms of the ligand densities.