TOTAL (50)

Problem 1: (10 points) page 1

A single E. coli bacterium starts growing at noon today with unrestricted food sources. At noon two days later:

- (a) Roughly how many E. coli bacteria will there be?
- (b) What will be their total mass?
- (c) How many C atoms will they contain?
- (d) Assuming that they are growing on a glucose ( $C_6H_{12}O_6$ ) medium, roughly what mass of glucose will have been consumed? (include metabolic energy requirements)
- (a) Take the doubling time to be 50 minutes (3000 s), so the number of generations is

$$\frac{2 \cdot 24 \cdot 60}{50} = 57.6$$
 and the number of cells at the end of 48 hours is  $2^{57.6} = 2.18 \times 10^{17}$  cells.

- (b) The mass of an E. coli is  $1 \text{ pg} = 10^{-12} \text{ g} = 10^{-15} \text{ kg}$ , so the total mass is 218 kg.
- (c) Each cell has about  $10^{10}$  C atoms, so the number of C atoms is  $2.18 \times 10^{27}$  carbon atoms.
- (d) The number of glucose consumed must at least give this number of carbons, so

$$\frac{2.18 \times 10^{27}}{6} = 3.64 \times 10^{26}$$
 glucose molecules. But, each glucose has

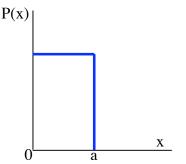
 $MW=6 \times 12 + 12 \times 1 + 6 \cdot 16 = 180$  Da, so the total glucose mass is  $3.64 \times 10^{26} (180)1.67 \times 10^{-27} = 109$  kg. But, there is also the glucose required for metabolic energy, so, I'd estimate about double this or glucose.

## Comment:

Where did the rest of the mass come from?

Partly, from atmospheric oxygen required to metabolize the glucose for energy: Note that each C needs two O's to metabolize to  $CO_2$  and only one of these is available from the glucose. Also, perhaps, from water, although some of the required water is generated metabolically.

A continuous random variable x is distributed uniformly over the interval [0,a] as shown at the right.



- (a) What is the average  $\langle x \rangle$  value of x?
- (b) What is the variance  $\sigma$  of x?

Suppose N independent variables  $\{x_n\}_{n=1}^N$ ,

each with the distribution  $P(x_n)$ , are added together, to form the sum  $X = \sum_{n=1}^{N} x_n$ .

- (c) What is the average value  $\langle X \rangle$ ?
- (d) What is the variance  $\sigma_N$  of X?
- (a) You can see from the figure that the distribution is symmetrical and centered at  $\frac{a}{2}$ .

Alternatively, notice that normalization requires that the height of the distribution is 1/a.

Then, calculate: 
$$\langle x \rangle = \frac{1}{a} \int_{0}^{a} dx \ x = \frac{1}{a} \cdot \frac{a^{2}}{2} = \frac{a}{2}$$
.

(b) 
$$\langle x^2 \rangle = \frac{1}{a} \int_0^a dx \, x^2 = \frac{a^2}{3}$$
, so  $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{a^2}{3} - \left(\frac{a}{2}\right)^2 = \frac{a^2}{12} \implies \sigma = \frac{a}{2\sqrt{3}}$ .

(c) 
$$\langle X \rangle = N \langle x \rangle = \frac{Na}{2}$$
.

(d) 
$$\langle X^2 \rangle = \langle (x_1 + x_2 + ...)^2 \rangle = N \langle x^2 \rangle + N(N-1) \langle x \rangle^2$$
, so

$$\sigma_N^2 = \left\langle X^2 \right\rangle - \left\langle X \right\rangle^2 = N \left\langle x^2 \right\rangle + N(N-1) \left\langle x \right\rangle^2 - \left(N \left\langle x \right\rangle\right)^2 = N \sigma^2 = \frac{Na^2}{12} \text{ and } \sigma_N = \frac{a}{2} \sqrt{\frac{N}{3}}.$$

Problem 3. (10 points)

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A three-state system has one state at energy  $\varepsilon_0$  and two at the higher energy  $\varepsilon_1 = \varepsilon_0 + \Delta$ . At what temperature T is the probability of finding energy  $\varepsilon_0$  equal to that of finding  $\varepsilon_1$ ? Hint: Your answer will be proportional to  $\Delta$ .

The probabilities of states at fixed T (canonical ensemble) are proportional to  $e^{-\frac{E_n}{k_BT}}$ . Thus the

probability of finding the ground state is  $\frac{1}{Z}e^{-\frac{\varepsilon_0}{k_BT}}$  while the probability of finding one of the *two* states

at 
$$\varepsilon_1$$
 is  $\frac{2}{Z}e^{-\frac{\varepsilon_1}{k_BT}}$ . These two become equal when  $e^{-\frac{\varepsilon_0}{k_BT}}=2e^{-\frac{\varepsilon_1}{k_BT}}\Rightarrow e^{\frac{\Delta}{k_BT}}=2$ , so  $T=\frac{\Delta}{k_B\ln 2}$ .

A statistical system s (not an ideal gas!) with N subsystems has an entropy function  $S(E,N) = Ak_B\sqrt{NE}$  (A>0 is a constant).

- (a) Suppose this system initially has energy  $E_s^0$ , what is its initial temperature  $T_s^0$  (as a function of N and  $E_s^0$ )?
- (b) Now consider an ideal monatomic gas of N particles in volume V with an initial energy  $E_g^0$ . What is the initial temperature  $T_g^0$  of this gas?
- (c) These two isolated systems are now put into thermal contact. What is the final temperature  $T^f$ , once the combined system comes to equilibrium?

Hint: If you do this problem right, you will end up with a quadratic equation. If you are short of time, display the equation but don't bother to solve it.

(a) The temperature is related to the energy derivative of S at constant E, so  $\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{Ak_B}{2} \sqrt{\frac{N}{E}}$  and

$$T_s^0 = \frac{2}{Ak_B} \sqrt{\frac{E_s^0}{N}}$$

(b) For the ideal gas, you know that  $E = \frac{3}{2}Nk_BT$ , so  $T_g^0 = \frac{2E_g^0}{3Nk_B}$ .

Alternatively, you can use the expression for the ideal-gas entropy,

 $S(E,V,N) = Nk_B \ln E^{3/2}$  + independent of E, and then calculate  $\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3}{2} \cdot \frac{Nk_B}{E}$ , which gives the same result (of course!).

(c) The key point is that the total energy  $E = E_s^0 + E_g^0$  of the isolated system cannot change, but energy will redistribute between the subsystems until the temperatures are equal. At that point

$$T_s = \frac{2}{Ak_B} \sqrt{\frac{E - E_g}{N}} = \frac{2E_g}{3Nk_B} = T_g$$

Square both sides and rearrange:  $E_g^2 + \frac{9N}{A^2}E_g - \frac{9N}{A^2}E = 0$ .

Solve for E<sub>g</sub>:  $E_g = \frac{N}{2} \left[ -\frac{9}{A^2} + \sqrt{\left(\frac{9}{A^2}\right)^2 + \frac{36E}{A^2N}} \right]$ . (the negative root is spurious)

Substitute this back into the formulas for either  $T_g$  or  $T_s$ , since they have to be the same:

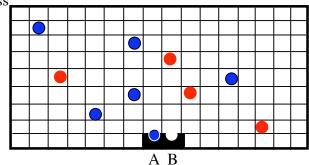
$$T^f = T_s = T_g = \frac{2E_g}{3Nk_B} = \frac{3}{k_B} \left[ -\frac{1}{A^2} + \sqrt{\left(\frac{1}{A^2}\right)^2 + \frac{4E}{9A^2N}} \right].$$

You can show that this will always lie between  $T_g^0$  and  $T_s^0$ 

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Consider a receptor which R can bind ligand molecules of two types, A (blue) and B (red) but not both, i.e., if the A-site is occupied (as for, example, in the figure), then the binding of a B releases the A, and vice versa. Thus, the receptor has three states, empty (R), binding an A (RA), and binding a B (RB). I

want you to consider the same kind of model of this process, as used in the book and in lecture, with the bulk "solution" represented by a lattice of N<sub>V</sub> sites. Suppose that the there are  $N_A$  molecules of type A, each of which has energy  $\varepsilon_S$ in solution and  $\varepsilon_A$  when bound and, similarly,  $N_B$ molecules of type B each of which has energy  $\varepsilon_S$  in solution and  $\varepsilon_{\scriptscriptstyle R}$  when bound. If the whole system is at temperature T, calculate the probability P<sub>A</sub> that an A particle is bound to the receptor.



Enumerate microstates: Three classes!

**Unbound:** Energy =  $(N_A + N_B)\varepsilon_s$ 

Number of states = 
$$\frac{N_V!}{N_A!N_B!(N_V - N_A - N_B)!}$$

**A Bound:** Energy = 
$$(N_A + N_B - 1)\varepsilon_s + \varepsilon_A$$

Number of states = 
$$\frac{N_V!}{(N_A - 1)!N_B!(N_V - N_A - N_B + 1)!} = \frac{N_V!}{N_A!N_B!(N_V - N_A - N_B)!} \cdot \frac{N_A}{(N_V - N_A - N_B + 1)!}$$

**B Bound:** Energy = 
$$(N_A + N_B - 1)\varepsilon_s + \varepsilon_B$$

Number of states = 
$$\frac{N_V!}{N_A!(N_B-1)!(N_V-N_A-N_B+1)!} = \frac{N_V!}{N_A!N_B!(N_V-N_A-N_B)!} \cdot \frac{N_B}{(N_V-N_A-N_B+1)!}$$

The probability of A being bound is:

$$P_{A} = \frac{e^{-\beta\left(\left(N_{A}+N_{B}-1\right)\varepsilon_{s}+\varepsilon_{A}\right)}\left[\#\ A\ states\right]}{e^{-\beta\left(\left(N_{A}+N_{B}\right)\varepsilon_{s}\right)}\left[\#\ 0\ states\right]+e^{-\beta\left(\left(N_{A}+N_{B}-1\right)\varepsilon_{s}+\varepsilon_{A}\right)}\left[\#\ A\ states\right]+e^{-\beta\left(\left(N_{A}+N_{B}-1\right)\varepsilon_{s}+\varepsilon_{B}\right)}\left[\#\ B\ states\right]}$$

Divide out common factors:

$$P_{A} = \frac{e^{-\beta\left((N_{A}+N_{B}-1)\varepsilon_{s}+\varepsilon_{A}\right)} \frac{N_{A}}{N_{V}-N_{A}-N_{B}+1}}{e^{-\beta\left((N_{A}+N_{B})\varepsilon_{s}\right)} + e^{-\beta\left((N_{A}+N_{B}-1)\varepsilon_{s}+\varepsilon_{A}\right)} \frac{N_{A}}{N_{V}-N_{A}-N_{B}+1} + e^{-\beta\left((N_{A}+N_{B}-1)\varepsilon_{s}+\varepsilon_{B}\right)} \frac{N_{B}}{N_{V}-N_{A}-N_{B}+1}}$$

$$P_{A} = \frac{N_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})}}{(N_{V}-N_{A}-N_{B}+1) + N_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})} + N_{A}e^{-\beta(\varepsilon_{B}-\varepsilon_{s})}} = \frac{c_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})}}{(1-c_{A}-c_{B}) + c_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})} + c_{B}e^{-\beta(\varepsilon_{B}-\varepsilon_{s})}},$$

$$P_{A} = \frac{N_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})}}{\left(N_{V}-N_{A}-N_{B}+1\right)+N_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})}+N_{A}e^{-\beta(\varepsilon_{B}-\varepsilon_{s})}} = \frac{c_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})}}{\left(1-c_{A}-c_{B}\right)+c_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})}+c_{B}e^{-\beta(\varepsilon_{B}-\varepsilon_{s})}},$$

where  $c_{\alpha} = \frac{N_{\alpha}}{N_{\text{tv}}}$  and the small term  $1/N_{\text{v}}$  has been dropped.

Alternatively, we could divide by the volume  $V = vN_V$  to get

$$P_{A} = \frac{n_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})}}{\left(\frac{1}{v}-n_{A}-n_{B}\right)+n_{A}e^{-\beta(\varepsilon_{A}-\varepsilon_{s})}+n_{B}e^{-\beta(\varepsilon_{B}-\varepsilon_{s})}}$$

Extended comment:

One or two people tried to do this from the grand canonical point of view.

No one got very far with it, but I thought I'd comment.

Yes, it is entirely possible to do it this way:

Looking at the "system" states only, the grand canonical weighting of states is  $P_n \sim e^{-\beta \left(E_n - \mu_A N_{A,n} - \mu_B N_{B,n}\right)}$ . Note that the A and B particles need separate chemical potentials, although in this special case they happen to be the same (see below).

There are only three such states, with energies  $0, \epsilon_A$ , and  $\epsilon_B$  and correspondingly

$$N_A = N_B = 0$$
;  $N_A = 1$ ,  $N_B = 0$ ; and  $N_A = 0$ ,  $N_B = 1$ .

Thus, the grand partition function (normalizing factor) is  $\Xi = 1 + e^{-\beta(\varepsilon_A - \mu_A)} + e^{-\beta(\varepsilon_B - \mu_B)}$ , so the probability

of the A-bound state is 
$$P_A = \frac{e^{-\beta(\varepsilon_A - \mu_A)}}{1 + e^{-\beta(\varepsilon_A - \mu_A)} + e^{-\beta(\varepsilon_B - \mu_B)}}$$
.

To go on from here, we need to find the A and B chemical potentials. This can be done is several ways, but the easiest is probably to look at the ligands in the canonical ensemble:

$$F(T,N_V,N_A,N_B) = -kT \ln Z$$
, with  $Z = \sum_n e^{-\beta E_n}$ . All the microstates here have the same energy,

 $E_n = (N_A + N_B)\varepsilon_s$ , but there are a lot of them, corresponding to the many different ways of putting  $N_A$  A's and  $N_B$  B's onto  $N_V$  lattice sites.

Counting them in the usual way gives a multiplicity of 
$$\frac{N_V!}{N_A!N_B!(N_V-N_A-N_B)!}$$
.

Thus, 
$$Z = \sum_{n} e^{-\beta E_n} = e^{-\beta (N_A + N_B)\varepsilon_s} \frac{N_V!}{N_A! N_B! (N_V - N_A - N_B)!}$$
.

Taking the log and using the Stirling formula gives finally,

$$F(N_A, N_B) = (N_A + N_B)\varepsilon_s + k_B T \left[ N_A \ln\left(\frac{N_A}{N_V}\right) + N_B \ln\left(\frac{N_B}{N_V}\right) + (N_V - N_A - N_B) \ln\left(\frac{N_V - N_A - N_B}{N_V}\right) \right], \text{ from } N_V = (N_A + N_B)\varepsilon_s + k_B T \left[ N_A \ln\left(\frac{N_A}{N_V}\right) + N_B \ln\left(\frac{N_B}{N_V}\right) + (N_V - N_A - N_B) \ln\left(\frac{N_V - N_A - N_B}{N_V}\right) \right], \text{ from } N_V = (N_A + N_B)\varepsilon_s + k_B T \left[ N_A \ln\left(\frac{N_A}{N_V}\right) + N_B \ln\left(\frac{N_B}{N_V}\right) + (N_V - N_A - N_B) \ln\left(\frac{N_V - N_A - N_B}{N_V}\right) \right], \text{ from } N_V = (N_A + N_B)\varepsilon_s + k_B T \left[ N_A \ln\left(\frac{N_A}{N_V}\right) + N_B \ln\left(\frac{N_B}{N_V}\right) + (N_V - N_A - N_B) \ln\left(\frac{N_V - N_A - N_B}{N_V}\right) \right], \text{ from } N_V = (N_V - N_A - N_B) \ln\left(\frac{N_B}{N_V}\right) + (N_V - N_A - N_B) \ln\left(\frac{N_B}{N_V}\right) + (N_V - N_A - N_B) \ln\left(\frac{N_V - N_A - N_B}{N_V}\right) \right]$$

which we can calculate 
$$\frac{\partial F}{\partial N_A} = \mu_A = \varepsilon_s + k_B T \left[ \ln c_A - \ln (1 - c_A - c_B) \right]$$
, which gives  $e^{\beta \mu_A} = e^{\beta \varepsilon_s} \left( \frac{c_A}{1 - c_A - c_B} \right)$ 

and similarly for B. When these results are substituted back into the grand canonical formula for  $P_A$ , we get back the previous result.

Notice that in this case the chemical potential for A depends on the density of A and the density of B. This is unlike what happened for the ideal gases and comes about because in this model the A's and B's have an important interaction between them: they are not allowed to sit on the same lattice site.