3.012 PS 9 : Bonding

1)
- Hamiltonian (in atomic units): $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$
($\frac{e^2}{4\pi\epsilon_0 a}$=1 $hartree$=1 $a.u.$=27.21 eV; a=1 $bohr$=1 $a.u.$=0.5292 × 10^{-10} m)

- Trial wavefunctions: $\Psi_\alpha = Ce^{-\alpha r}$ (C is a normalization constant)

- Variational parameter: α

The expectation value for the total energy of the trial wavefunction (which we want to minimize with respect to the variational parameter to obtain the energetically optimal trial wavefunction) can be expressed as:

$$E_\alpha = \frac{\langle \Psi_\alpha | \hat{H} | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle} \tag{1}$$

$$E_\alpha = \frac{\langle \Psi_\alpha | -\frac{1}{2}\nabla^2 | \Psi_\alpha \rangle + \langle \Psi_\alpha | -\frac{1}{r} | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle} \tag{2}$$

The terms in the preceding expression can be calculated as follows:

$$\langle \Psi_\alpha | -\frac{1}{2}\nabla^2 | \Psi_\alpha \rangle = -\frac{1}{2}\int_{r=0}^{r=\infty}\int_{\theta=0}^{\theta=\pi}\int_{\phi=0}^{\phi=2\pi} \Psi_\alpha^*(r)\nabla^2\Psi_\alpha(r)r^2 sin(\theta)drd\theta d\phi$$

$$\langle \Psi_\alpha | -\frac{1}{2}\nabla^2 | \Psi_\alpha \rangle = -\frac{1}{2}\int_{r=0}^{r=\infty} \Psi_\alpha^*(r)\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\Psi_\alpha(r)4\pi r^2 dr$$

(because Ψ_α does not depend on θ and ϕ)

$$\langle \Psi_\alpha | -\frac{1}{2}\nabla^2 | \Psi_\alpha \rangle = -\frac{4\pi C^2}{2}\int_{r=0}^{r=\infty} e^{-\alpha r}\frac{\alpha^2 r^2 - 2\alpha r}{r^2}e^{-\alpha r}r^2 dr$$

$$\langle \Psi_\alpha | -\frac{1}{2}\nabla^2 | \Psi_\alpha \rangle = -\frac{4\pi C^2}{2}\int_{r=0}^{r=\infty} (\alpha^2 r^2 - 2\alpha r)e^{-2\alpha r} dr$$

$$\langle \Psi_\alpha | -\frac{1}{2}\nabla^2 | \Psi_\alpha \rangle = -\frac{4\pi C^2}{2}(\alpha^2\frac{2!}{(2\alpha)^3} - 2\alpha\frac{1!}{(2\alpha)^2})$$

(from Appendix C.2. Mortimer)
As a result:

$$\langle \Psi_\alpha | -\frac{1}{2}\nabla^2 | \Psi_\alpha \rangle = +\frac{\pi C^2}{2\alpha} \tag{3}$$

Similarly,

$$\langle \Psi_\alpha | -\frac{1}{r} | \Psi_\alpha \rangle = -\int_{r=0}^{r=\infty}\int_{\theta=0}^{\theta=\pi}\int_{\phi=0}^{\phi=2\pi} \Psi_\alpha^*(r)\frac{1}{r}\Psi_\alpha(r)r^2 sin(\theta)drd\theta d\phi$$

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$$\langle \Psi_\alpha | -\frac{1}{r} | \Psi_\alpha \rangle = -4\pi C^2 \int_{r=0}^{r=\infty} e^{-2\alpha r} r\, dr$$

$$\langle \Psi_\alpha | -\frac{1}{r} | \Psi_\alpha \rangle = -4\pi C^2 \frac{1!}{(2\alpha)^2}$$

$$\langle \Psi_\alpha | -\frac{1}{r} | \Psi_\alpha \rangle = -\frac{\pi C^2}{\alpha^2} \tag{4}$$

$$\langle \Psi_\alpha | \Psi_\alpha \rangle = -\int_{r=0}^{r=\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \Psi_\alpha^*(r)\Psi_\alpha(r) r^2 sin(\theta) dr d\theta d\phi$$

$$\langle \Psi_\alpha | \Psi_\alpha \rangle = 4\pi C^2 \int_{r=0}^{r=\infty} e^{-2\alpha r} r^2\, dr$$

$$\langle \Psi_\alpha | \Psi_\alpha \rangle = 4\pi C^2 \frac{2!}{(2\alpha)^3}$$

$$\langle \Psi_\alpha | \Psi_\alpha \rangle = +\frac{\pi C^2}{\alpha^3} \tag{5}$$

Consequently,

$$E_\alpha = \frac{\frac{\pi C^2}{2\alpha} - \frac{\pi C^2}{\alpha^2}}{\frac{\pi C^2}{\alpha^3}} \tag{6}$$

$$\underline{E_\alpha = \frac{1}{2}\alpha^2 - \alpha} \tag{7}$$

To obtain the energetically optimal trial wavefunction $\Psi_{\alpha min}$, we have to find the value $\alpha = \alpha_{min}$ which minimizes $E_\alpha = \frac{1}{2}\alpha^2 - \alpha$:

$$\frac{dE_\alpha}{d\alpha} = \alpha - 1 = 0 \tag{8}$$

Thus, we obtain the following solution:

$$\alpha_{min} = 1 \tag{9}$$

$$E_{\alpha_{min}} = -\frac{1}{2}\ hartree \tag{10}$$

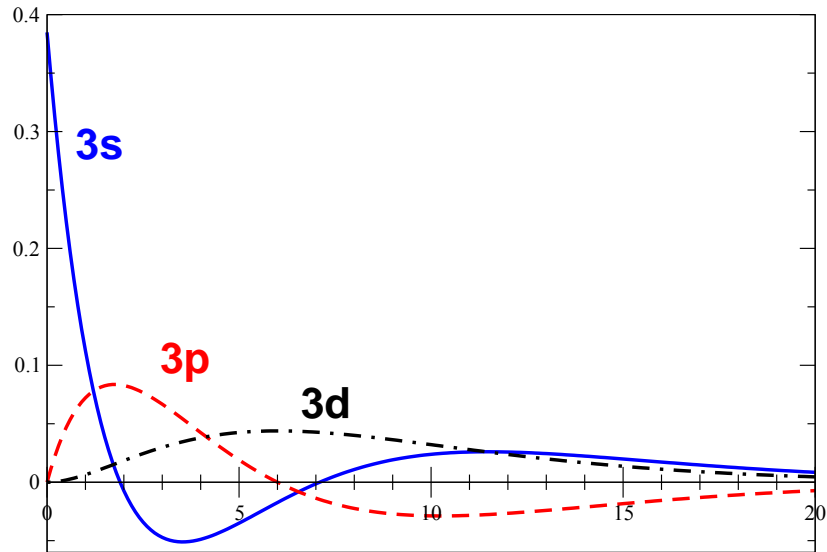$$\underline{\Psi_{\alpha_{min}} = Ce^{-r}} \tag{11}$$

[To evaluate C, we use the normalization condition:

$$\langle \Psi_{\alpha_{min}} | \Psi_{\alpha_{min}} \rangle = 1 \tag{12}$$

$$\frac{\pi C^2}{1^3} = 1 \tag{13}$$

Consequently, $C = \frac{1}{\sqrt{\pi}}$ and $\Psi_{\alpha_{min}} = \frac{1}{\sqrt{\pi}}e^{-r}$]

2

2) The radial components of the $3s$, $3p$, $3d$ orbitals for the hydrogen atom:

From the preceding graphs two remarks can be made:
- the radial function $R_{nl}(r)$ displays $n - l - 1$ nodes (nodes at $R = 0$ excluded);
- the radial function $R_{nl}(r)$ behaves as r^l when $r \approx 0$.

Moreover, the number of nodal surfaces due to the angular component $Y_{lm}(\theta, \phi)$ is l : $l - m$ due to $\Theta_{lm}(\theta)$; m due to $\Phi_{mx}(\phi)$ (or $\Phi_{my}(\phi)$).
(Cf. lecture notes or recitation 3)

The number and nature of the nodal surfaces for the $3s$, $3p$, $3d$ are listed below:

	n	l	m	radial	angular	total
					nodal surfaces	
Ψ_{nlmx} or Ψ_{nlmy}	n	l	m	$n-l-1$	l	$n-1$
3s	3	0	0	2 spheres	0	2
3p0	3	1	0	1 sphere	1 horizontal plane	2
3p1	3	1	1	1 sphere	1 vertical plane	2
3d0	3	2	0	0	2 cones	2
3d1	3	2	1	0	1 horizontal plane +1 vertical plane	2
3d2	3	2	2	0	2 vertical planes	2

3) Two main factors determine the angles between atoms in CH_4, NH_3 and H_2O:
- *the nature of the sp hybridization;*
- *the number of lone pairs.*

In these three molecules, the $2s$ and the three $2p$ atomic orbitals of the carbon atom hybridize to form four sp^3 orbitals. The structure around C is close to tetrahedral and the bond angle is aproximately 109.5^o ($\approx cos^{-1}(1/3)$).

The presence of valence electron lone pairs slightly modifies this tetrahedral structure. Indeed, the repulsive interaction between lone pairs and bond pairs are not equal:

$repulsion(lone, lone) > repulsion(lone, bond) > repulsion(bond, bond)$.

As a result, when the number of lone pairs increases, the bond angle (which involves two bond pairs) decreases.

molecule	number of valence electron pairs	number of lone pairs	hybridization, structure	bond angle
CH_4	4	0	sp^3, tetrahedral	109.5^o
NH_3	4	1	sp^3, tetrahedral	107°
H_2O	4	2	sp^3, tetrahedral	104.5^o

5) The change in bond length between C_2H_6, C_2H_4 and C_2H_2 can be explained by the number of electron pairs involved in the $C - C$ bonding (bond order): the bond length decreases as the bond order increases. This number is related to the nature of the sp hybridization.

As an example, in C_2H_4, the hybridization is: sp^2. Two of the three sp^2 orbitals of each C atom are used to attach the two H atoms ($H - C$ bonding state). The remaining sp^2 orbitals hybridize to form a σ bonding orbital. The last p orbitals not used in the sp^2 hybridization (orbitals along the direction normal to the plane of the molecule) combine constructively to form a π bonding state.

The results are summarized in the following table:

molecule	number of H bound to each C	$C - C$ bonds	hybridization, structure	bond length
C_2H_6	3	1 σ	sp^3, tetrahedral	1.543 Å
C_2H_4	2	1 σ, 1 π	sp^2, trigonal planar	1.353 Å
C_2H_2	1	1 σ, 2 π	sp^1, linear	1.207 Å

THERMODYNAMICS

1. **Phase separation of a regular solution**. Given below is thermodynamic data for an A-B solid solution that exhibits regular solution behavior, with a miscibility gap in the solid state. You have a sample with composition $X_B = 0.15$ which is cooled from very high temperatures to 250 K.

$$\mu_{A,o} = -2,000\frac{J}{mole}$$

$$\mu_{B,o} = -1,000\frac{J}{mole}$$

$$\Omega = 7,000\frac{J}{mole}$$

As a reminder, you can derive the molar free energy of solution for the regular solution from the molar free energy of mixing and the molar free energy of the heterogeneous A-B mixture:

$$\Delta\overline{G}^{mix,rs} = \overline{G}^{RS} - \overline{G}^{heter}$$

$$\overline{G}^{RS} = \Delta\overline{G}^{mix,rs} + \overline{G}^{heter} = \Omega X_A X_B + RT\left[X_A \ln X_A + X_B \ln X_B\right] + \mu_{A,o}X_A + \mu_{B,o}X_B$$

a.   What is the critical temperature for this system?

The critical temperature marks the first point on the phase diagram as temperature is lowered where phase separation occurs (at the top center of the miscibility gap). The critical point is identified by finding the point at the center of the composition axis ($X_B = 0.5$) where the second derivative of the free energy goes to zero (i.e., at the onset of the 'humped' shape in the free energy):

$$\left(\frac{\partial^2 \Delta\overline{G}^{mix,RS}}{\partial X_B^2}\right)\bigg|_{X_B=0.5} = 0$$

Plugging in the expression for the regular solution free energy of mixing and solving for T, we arrive at the expression given in class for the critical temperature:

$$T_{crit} = \frac{\Omega}{2R} = \frac{7000}{2(8.3144)} = 420.9K$$

b.   What are the locations (X_B values) of the spinodals and the phase boundaries (boundaries between the miscilibility gap and pure α_1, α_2 phases) for this regular solution at the given temperature?

The phase boundaries and spinodals are determined by examining the free energy vs. composition curve. At a temperature below the criticial point (within the miscibility gap), the phase boundaries are set by the ends of the common tangent that runs between the 'humps' of the free energy curve, while the spinodals are set by the saddlepoints on the plot where the free energy's curvature changes sign. These points are illustrated on the diagram below.
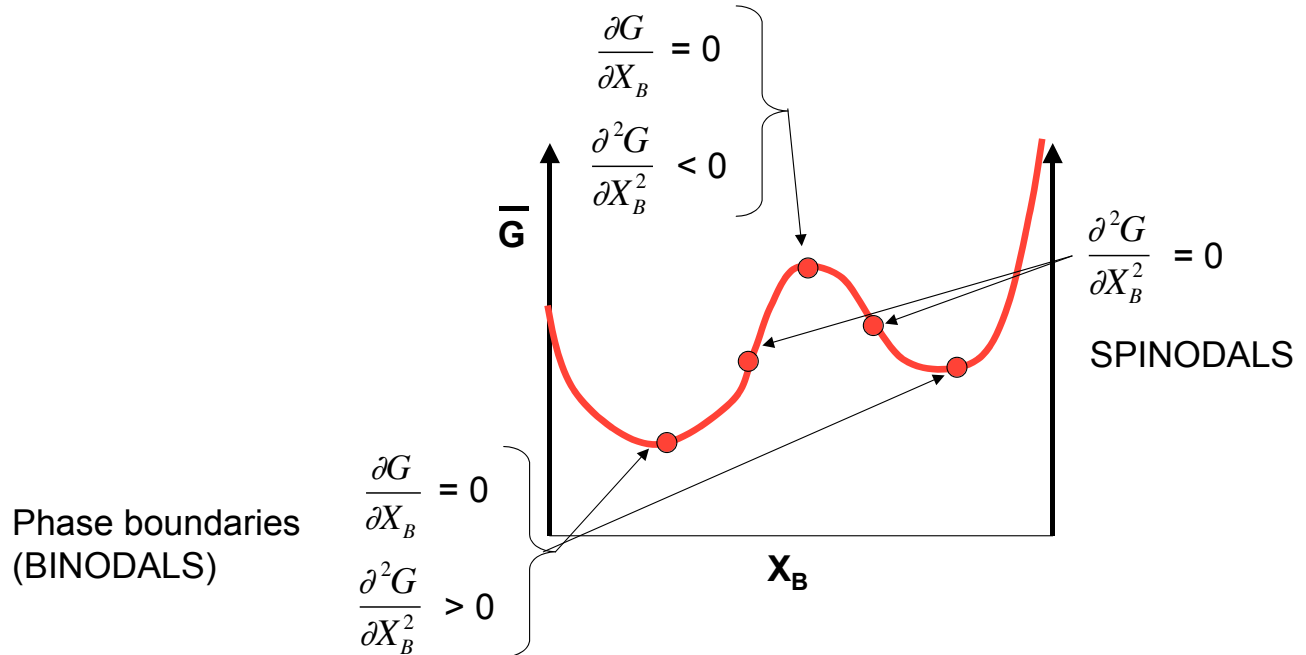
Mathematically, the phase boundaries are set by the points where the first derivative of the free energy of the solution is zero. We can derive the analytic solution to this situation:

$$\frac{\partial \overline{G}^{RS}}{\partial X_B} = \frac{\partial}{\partial X_B}\left[\Omega(1-X_B)X_B + \mu_{A,o}(1-X_B) + \mu_{B,o}X_B + RT\left\{(1-X_B)\ln(1-X_B) + X_B \ln X_B\right\}\right] = 0$$

We write the free energy above completely in terms of X_B to calculate the partial derivative. Taking the derivative, we can simplify the expression:

$$\frac{\partial \overline{G}^{RS}}{\partial X_B} = \Omega - 2\Omega X_B - \mu_{A,o} + \mu_{B,o} + RT \ln\frac{X_B}{(1-X_B)} = 0 \text{ at the phase boundaries}$$

The spinodal points will be identified by looking at the second derivative of the free energy:

$$\frac{\partial^2 \overline{G}^{RS}}{\partial X_B^2} = -2\Omega + RT\left[\frac{1}{X_B} + \frac{1}{(1-X_B)}\right] = 0 \text{ at the spinodal points}$$

It is instructive to look at a plot of all 3 expressions: the molar free energy of the solution, its first derivative, and its second derivative vs. X_B at the given temperature:
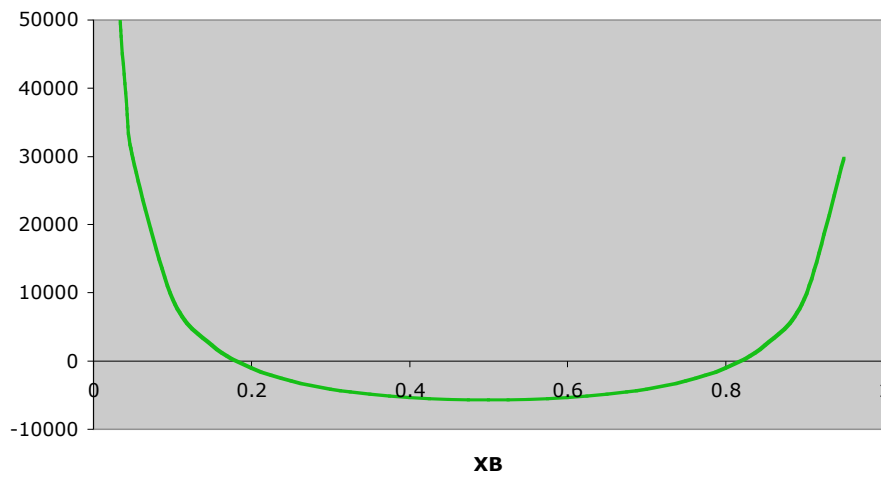
molar free energy of the regular solution

slope

## curvature

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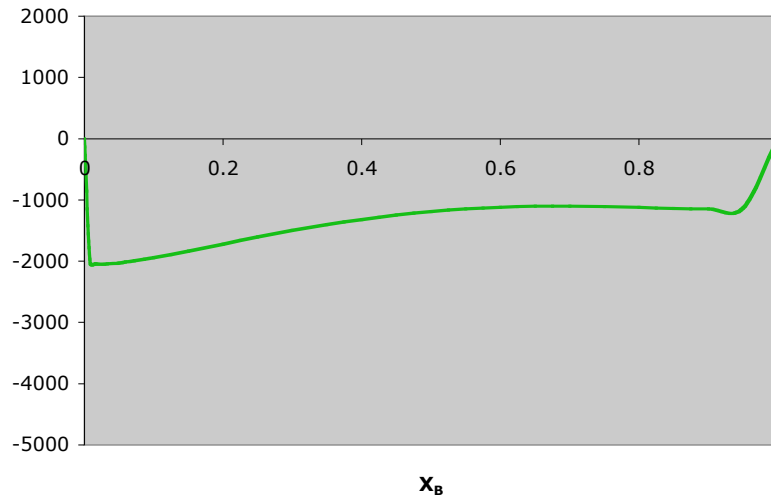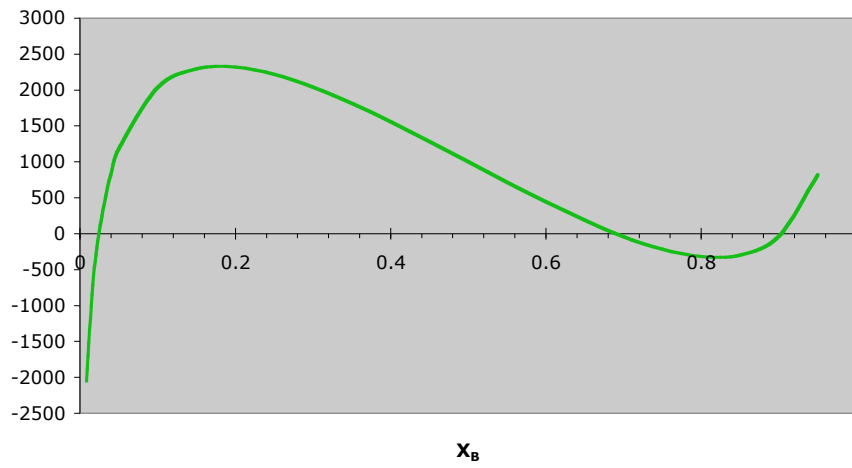
We can note several characteristics from the curves: The free energy curve displays the expected 'W' shape for a regular solution below the critical temperature. The slope curve crosses zero at 3 points as X_B varies from 0 to 1: once at each of the free energy minima, and once at the local maximum in the hump between the two valleys of the 'W'. The curvature passes through zero at two locations as expected, and is symmetric about $X_B = 0.5$. Now, to answer the posed question, the approximate phase boundary and spinodal locations from these graphs are:

Phase boundaries: $X_B = 0.025$ and $X_B = 0.9$
Spinoodals: $X_B = 0.18$ and $X_B = 0.82$

   c. At the given temperature and composition, will this system phase separate by nucleation and growth or by spinodal decomposition? Show why.

The mechanism of phase separation- nucleation and growth vs. spinodal decomposition- for binary systems cooled a temperature within the phase boundaries is determined by the location of the system on the composition/temperature diagram. If the composition falls inside the phase boundaries but outside the spinodal boundaries, nucleation and growth occurs; inside the spinodals, spinodal decomposition is the mode of phase separation. A the given composition, $X_B = 0.15$, we are between the left-hand phase boundary and the left-hand spinodal, indicating that nucleation and growth will occur.

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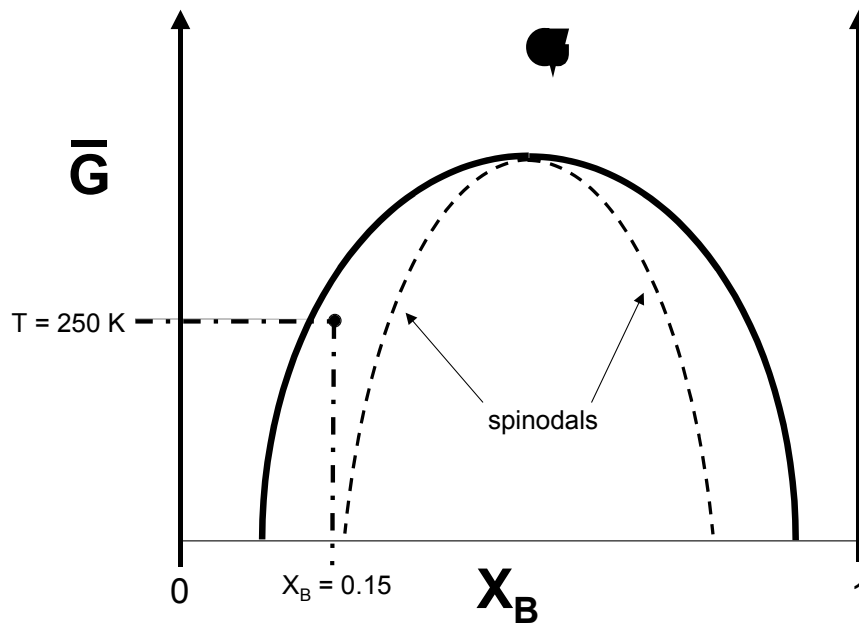
2. **Two-state quantum systems**. Suppose you have a collection of N non-interacting molecules that are indistinguishable (and identical). Each molecule resides in one of two microstates: a ground state with energy 0, and an excited state with energy ε_0.

    a. What is the molecular partition function for this system?

The partition function is a sum of Boltzmann factors for each of the possible molecular states. There are only two states for each molecule, with energies 0 and ε_0, respectively:

$$q = \sum_{i=1}^{\text{all molecular states}} e^{-\frac{\varepsilon_i}{kT}} = e^{-\frac{0}{kT}} + e^{-\frac{\varepsilon_0}{kT}} = 1 + e^{-\frac{\varepsilon_0}{kT}}$$

    b. What is the partition function of the entire system of N molecules?

Because the given state is composed of non-interacting molecules, the system partition function is obtained by simply as a product of N single-molecule partition functions. In addition, because the molecules are indistinguishable, we correct for over-counting total system states that are indistinguishable by dividing by N!:

$$Q = \frac{q^N}{N!} = \frac{\left(1 + e^{-\frac{\varepsilon_0}{kT}}\right)^N}{N!}$$

    c. What is the internal energy of this system as the temperature approaches infinity?

The internal energy is obtained from the ensemble average energy. The most convenient route to obtain the ensemble average energy is through the direct relationship between U and the system partition function:

$$U = <E> = kT^2 \frac{\partial \ln Q}{\partial T} = kT^2 \frac{\partial}{\partial T}\left[\ln\left(\frac{\left(1 + e^{-\varepsilon_o/kT}\right)^N}{N!}\right)\right] = kT^2 \frac{\partial}{\partial T}\left[N\ln\left(1 + e^{-\varepsilon_o/kT}\right) - \ln N!\right]$$

$$U = kT^2 N \frac{\left(\frac{\varepsilon_o}{kT^2}\right)e^{-\varepsilon_o/kT}}{\left(1 + e^{-\varepsilon_o/kT}\right)}$$

As the temperature approaches infinity, the expression reduces to:

$$U = kT^2 N \frac{\left(\frac{\varepsilon_o}{kT^2}\right)}{(1+1)} = N\frac{\varepsilon_o}{2}$$

    d. Using the molecular partition function, determine what temperature gives a probability for a molecule to reside in the excited state equal to 1/2. (Hint: The answer will seem

unusual- it is a unique property of a two-state system. But you should readily be able to solve for T!)

We are asked to look at a molecular state probability:

$$p_{\varepsilon_o} = \frac{1}{2}$$

This is the probability that a given molecule is in the excited state with energy $\varepsilon = \varepsilon_o$:

$$p_{\varepsilon_o} = \frac{1}{2} = \frac{e^{-\frac{\varepsilon_o}{kT}}}{q} = \frac{e^{-\frac{\varepsilon_o}{kT}}}{\left(1 + e^{-\frac{\varepsilon_o}{kT}}\right)}$$

$$\frac{1}{2} = \frac{e^{-\frac{\varepsilon_o}{kT}}}{\left(1 + e^{-\frac{\varepsilon_o}{kT}}\right)}$$

We can rearrange this expression to solve for T:

$$\frac{1}{2} = \frac{1}{\left(e^{\frac{\varepsilon_o}{kT}} + 1\right)}$$

$$\left(e^{\frac{\varepsilon_o}{kT}} + 1\right)\frac{1}{2} = 1$$

$$e^{\frac{\varepsilon_o}{kT}} = 1$$

For the last equation to be true, T must be infinity. This bizarre result is a characteristic of two-state quantum systems, and matches the prediction for the internal energy derived in part (c).

3. **Predicting molecular collapse of a polymer chain at cold temperatures**[DJI1]. Let's determine the thermodynamic properties of a 6-repeat unit polymer chain, modeled as a set of 6 connected beads. The links between each bead (covalent bonds in the real polymer) are flexible and allow the chain to reside in numerous possible microstates, which are enumerated in the figure below. Within these microstates, the internal energy of the chain is *greater* when there are no bead-bead contacts (contacts between beads which are *not* covalently linked to one another). The microstates have 3 different possible energies, based on the number of bead-bead contacts present: states with no contacts have an energy $2\varepsilon_o$, states with 1 bead-bead contact have an energy ε_o, and states with 2 bead-bead contacts have an energy 0. As shown in the figure below, there are 4 states with 2 contacts, 11 states with 1 contact, and 21 states with zero contacts. Use this simple model to answer the following questions:

   a. What is the partition function for this 6-unit polymer?

The molecular partition function for the polymer sums over the states; we can group together the Boltzmann factors for states with the same energy:

$$q = 4\left(e^{-\frac{0}{kT}}\right) + 11\left(e^{-\frac{\varepsilon_o}{kT}}\right) + 21\left(e^{-\frac{2\varepsilon_o}{kT}}\right) = 4 + 11\left(e^{-\frac{\varepsilon_o}{kT}}\right) + 21\left(e^{-\frac{2\varepsilon_o}{kT}}\right)$$

   b. What is the probability of the polymer being in a state with energy 0, ε_o, or 2 ε_o? (Hint: you want to know the probability of being in *any of the states* with the energy of interest, not just the probability of being in *one specific state* of that energy).

We know the probability of being in *one specific* microstate is given by the ratio of the Boltzmann factor over the partition function:

$$p_j = \frac{e^{-\frac{\varepsilon_j}{kT}}}{q}$$

Now, to get the total probability for finding the polymer in any of the different conformations we must sum the probabilities for each microstate that has the same energy:

$$p_{\varepsilon=0} = 4p_0 = 4\left(\frac{e^{-\frac{0}{kT}}}{q}\right) = \frac{4}{q}$$

$$p_{\varepsilon=\varepsilon_o} = 11p_0 = 11\left(\frac{e^{-\frac{\varepsilon_o}{kT}}}{q}\right)$$

$$p_{\varepsilon=2\varepsilon_o} = 21p_0 = 21\left(\frac{e^{-\frac{2\varepsilon_o}{kT}}}{q}\right)$$

c. Calculate the internal energy of the polymer chain as a function of temperature.

We again make use of the relationship between the ensemble average energy and the partition function:

$$U = <E> = kT^2 \frac{\partial \ln Q}{\partial T} = kT^2 \frac{\partial}{\partial T}\left[\ln\left(4 + 11\left(e^{-\frac{\varepsilon_o}{kT}}\right) + 21\left(e^{-\frac{2\varepsilon_o}{kT}}\right)\right)\right]$$

$$\therefore U = kT^2\left(\frac{\dfrac{11\varepsilon_o e^{-\frac{\varepsilon_o}{kT}}}{kT^2} + \dfrac{42\varepsilon_o e^{-\frac{2\varepsilon_o}{kT}}}{kT^2}}{q}\right) = \varepsilon_o e^{-\frac{\varepsilon_o}{kT}}\left(\frac{11 + 42e^{-\frac{\varepsilon_o}{kT}}}{q}\right)$$

d. Calculate the value of the critical temperature T_c, where the polymer is 50% likely to be in one of the fully collapsed (2-contact) states. You do not need to solve the final equation- simply reduce the required relationship as much as possible (a graphical/numerical solution is required to obtain the exact value of T_c).

The probability of finding the system in one of the fully collapsed states is:

$$P_{\text{one collapsed state}} = \frac{e^{-\frac{0}{kT}}}{q} = \frac{1}{q}$$

There are 4 different fully collapsed states, and we want to know the temperature where the total probability is 50%:

$$p_{collapsed} = 4\,p_{\text{one collapsed state}} = \frac{4}{q} = \frac{4}{\left(4 + 11e^{-\frac{\varepsilon_o}{kT}} + 21e^{-\frac{2\varepsilon_o}{kT}}\right)}$$

$$\frac{1}{2} = \frac{4}{\left(4 + 11e^{-\frac{\varepsilon_o}{kT}} + 21e^{-\frac{2\varepsilon_o}{kT}}\right)}$$

The last equality must be satisfied at T = T$_{crit}$. To find the critical temperature, we would solve for T in the last equality, which could be done numerically.

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