Name: BE.011 Final Exam Answers Spring '03

BE.011/2.993J
Spring 2003
FINAL EXAM
May 19, 2003

You have 3 hours for this exam.

CLOSED BOOK
4 pages of notes allowed

1. (60 points)	
2. (20 points)	
3. (10 points)	
4. (40 points)	
5. (65 points)	
6. (30 points)	
total (225 points)	

Some constants you may need:

$k = 1.38 \times 10^{-23}$ J K^{-1}

$R = 8.314$ J K^{-1} mol^{-1}

$h = 6.626 \times 10^{-34}$ J s

1 atomic mass unit (amu) = 1.66×10^{-27} kg

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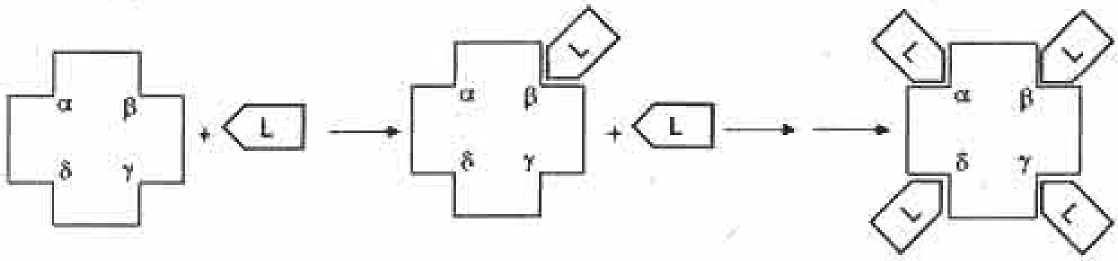
1.) **(60 points total)** The protein below has four binding sites (α, β, γ, δ) for the ligand L (look familiar?). Assume that the association and dissociation constants are equal.



It has energies associated with each macrostate L, where L is the # of ligands:

#L	energy
0	8ε
1	4ε
2	2ε
3	1ε
4	0

1a.) (10 points) Plot an energy level diagram, including all microstates. Label values on the y axis in terms of the energy unit ε.

Now we need to take into account the degeneracy of each level

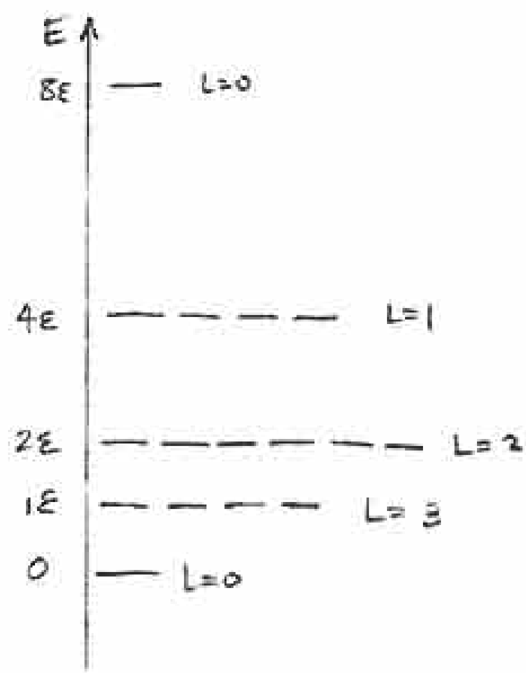
for $L=0$, $W_{L=0} = \frac{4!}{0!\,4!} = 1$

$L=1$ $\quad W_{L=1} = \frac{4!}{3!\,1!} = 4$

$L=2$ $\quad W_{L=2} = \frac{4!}{2!\,2!} = 6$

$L=3$ $\quad W_{L=3} = \frac{4!}{1!\,3!} = 4$

$L=4$ $\quad W_{L=4} = \frac{4!}{4!\,0!} = 1$



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1b.) (10 points) Write down an expression for the partition function q. Calculate its value at a temperature where kT = 3ε.

$$q = \sum_{l=0}^{4} W_l \, e^{-\varepsilon_l/kT} = 1\cdot e^{-8\varepsilon/kT} + 4e^{-4\varepsilon/kT} + 6e^{-2\varepsilon/kT} + 4e^{-\varepsilon/kT} + 1$$

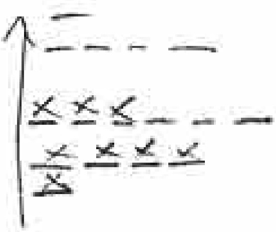
if $kT = 3\varepsilon$

$$q = e^{-8/3} + 4e^{-4/3} + 6e^{-2/3} + 4e^{-1/3} + 1$$

$$= 0.06948 + 1.05 + 3.08 + 2.866 + 1 = \boxed{8.065 = q}$$

1c.) (5 points) What is the highest macrostate that is populated at this temperature kT = 3ε? How many of the microstates in this macrostate are populated?

From above, about 8 states are available — this puts the highest level accessible as the L=2 state — about half of these are populated:



where "x" is an occupied state.

1d.) (10 points) Calculate p_L for L = 0,1,2,3,4 at a temperature where kT = 3ε. What is $\Sigma_L p_L$?

$$p_l = \frac{W_l \, e^{-\varepsilon_l/kT}}{q}, \quad q = 8.065 \text{ at this temp.}$$

$$p_0 = \frac{1e^{-8/3}}{8.065} = 8.6\times10^{-3}$$

$$p_1 = \frac{4e^{-4/3}}{8.065} = 0.130$$

$$p_2 = \frac{6e^{-2/3}}{8.065} = 0.382$$

$$p_3 = \frac{4e^{-1/3}}{8.065} = 0.355$$

$$p_4 = \frac{1e^{0}}{8.065} = 0.124$$

$$\sum_L p_L = 8.6\times10^{-3} + 0.130 + 0.382 + 0.355 + 0.124$$

$= 1$ ✓ as it should! (credit also given for $\sum_L L \cdot p_L$)

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1e.) (10 points) Calculate <E> at a temperature where kT = 3ε (you can leave it in terms of ε).

$$\langle E \rangle = \sum_{\ell} \varepsilon_{\ell} p_{\ell} = 8\varepsilon(8.6\times10^{-3}) + 4\varepsilon(0.130) + 2\varepsilon(0.382) + \varepsilon(0.355) + 0$$

$$\boxed{\langle E \rangle = 1.71\,\varepsilon}$$

1f.) (5 points) What is the entropy, S, at a temperature where kT = 3ε?

$$S = -k \sum_{\ell} p_{\ell} \ln p_{\ell}$$

$$= -k\left[0.124(\ln 0.124) + 0.355(\ln 0.355) + 0.382(\ln 0.382) + 0.130\ln(0.130) + 8.6\times10^{-3}(\ln 8.6\times10^{-3})\right]$$

$$\boxed{S = 1.3k}$$

1g.) (5 points) What is the value of q as T→∞? then $e^{-()/kT} \approx e^{-0} = 1$

$$q = \sum_{\ell} W_{\ell} \cdot e^{-\varepsilon_{\ell}/kT} = 1e^{-0} + 4e^{-0} + 6e^{-0} + 4e^{-0} + 1$$

$$= 1 + 4 + 6 + 4 + 1$$

$$\boxed{q = 16} \text{ as } T \to \infty$$

all states become accessible.

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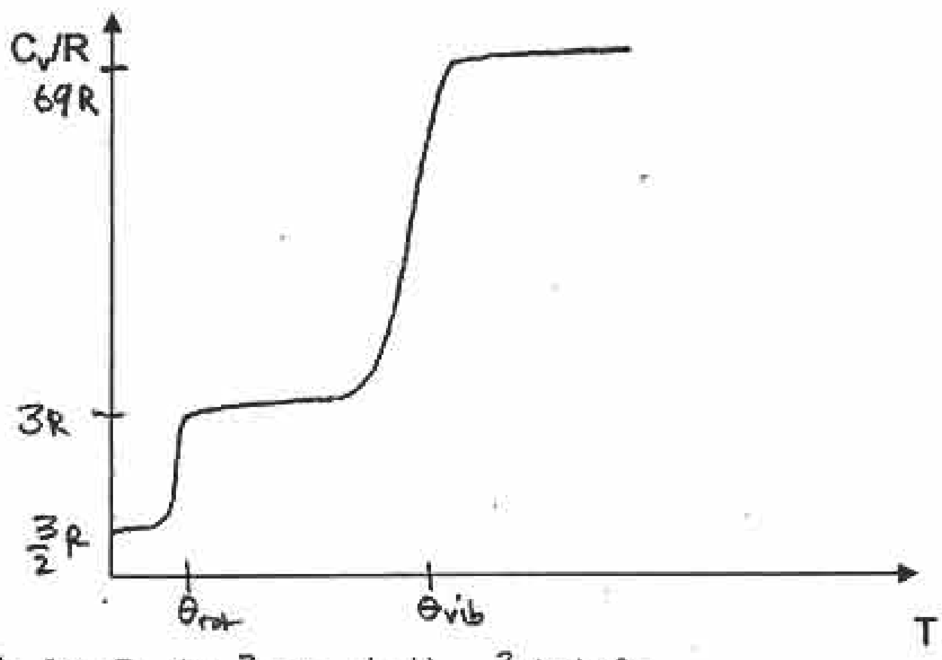
1h.) (5 points) What is S as T→∞?

$$S = -k\sum_i p_i \ln p_i = -k\left[\frac{1}{16}\ln\left(\frac{1}{16}\right) + \frac{4}{16}\ln\left(\frac{4}{16}\right) + \frac{6}{16}\ln\left(\frac{6}{16}\right) + \frac{4}{16}\ln\left(\frac{4}{16}\right) + \frac{1}{16}\ln\left(\frac{1}{16}\right)\right]$$

$\boxed{S = 1.4k}$ as $T \to \infty$

2.)**(20 points total)** Heat capacity of a molecule
You have the molecule glucose, which has 66 degrees of vibrational freedom. Plot its heat capacity as a function of temperature, making sure to denote on the plot

- values for heat capacity (in units of R) on the y axis
- where the rotational and vibrational temperatures, θ_{rot} and θ_{vib}, are on the x-axis.



3 translational D.O.F. ⇒ $\frac{3}{2}kT$ to U, $\underline{\frac{3}{2}R \text{ to } C_V}$

3 rotational D.O.F (rotate about 3 axes: I_a, I_b, I_c) ⇒ $\frac{3}{2}kT$ to U, $\underline{\frac{3}{2}R \text{ to } C_V}$

66 vibrational D.O.F. ⇒ 66 kT to U (1kT each), 66R to C_V

$\theta_{vib} > \theta_{rot} > \theta_{trans}$

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3.) **(10 points total)** Ribonuclease A is a protein that has 124 amino acids.

3a.) (5 points) What is the probability that this sequence is unique?

20 amino acids so

$$\frac{1}{20^{124}}$$

3b.) (5 points) Assume that residues 1-20 are conserved (exactly the same). How many different homologies are possible for RNase A?

so only $124 - 20 = 104$ can change

20^{104} variations possible.

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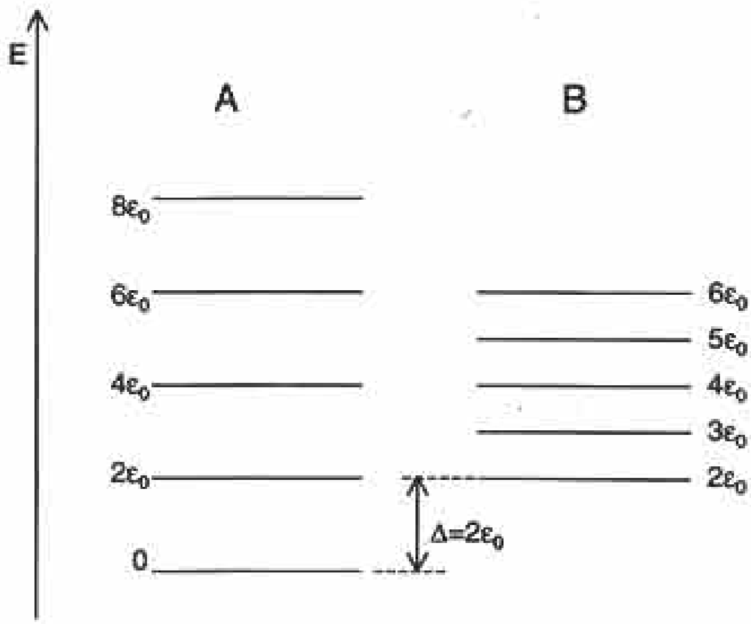
4.) (**40 points total**) Equilibrium between two states. The reaction

$$A \longrightarrow B$$

has the equilibrium constant K. The energy levels for A and B are shown below:



A has a fixed energy level spacing of $2\varepsilon_0$, with a ground state energy of 0. B has a fixed energy spacing of ε_0 with a ground state energy of $2\varepsilon_0$.

4a.) (10 points) Calculate K for the reaction, assuming $kT=2\varepsilon_0$.

$$q_B' = e^{-1} + e^{-1.5} + e^{-2} + e^{-2.5} + e^{-3} = e^{-1}\cdot q_B = 0.8582$$

$$q_A' = 1 + e^{-1} + e^{-2} + e^{-3} + e^{-4} = q_A = 1.5713$$

$$K = \frac{q_B'}{q_A'} = \frac{0.8582}{1.5713} = \underline{\underline{0.5462}}$$

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4b.) (10 points) What is K as $T \rightarrow \infty$?

As $T \rightarrow \infty$, all microstates equally populated. Since A & B both have 5 microstates

$K \rightarrow 1$

4c.) (5 points) What side of the reaction is favored as $T \rightarrow 0$?

$\underline{\underline{A}}$ since it has the lowest energy microstate.

4d.) (10 points) Now suppose the ground state energy of B was also 0 (i.e., Δ=0). Calculate K using kT=2ε_0 gain.

$$K = \frac{q_B}{q_A} = \frac{e q_B'}{q_A} = \frac{0.8582e}{1.5713} = 0.5462e = \underline{\underline{1.4846}}$$

4e.) (5 points) Let's pretend A$\longrightarrow$B is an isomerization reaction, i.e., a molecule changing only in shape such as Helix$\longrightarrow$ Coil, and that the energy levels are vibrational. Which form of the molecule has stiffer bonds (higher bond spring constant, k)?

Form A.

$\Delta\varepsilon = h\nu$

$\Delta\varepsilon_A = 2\varepsilon_0 > \varepsilon_0 = \Delta\varepsilon_B$

$\therefore \nu_A > \nu_B$

Springs with higher k vibrate faster since ~~it requires more ore~~ maximum extension is smaller.

$\therefore$ A has stiffer bonds.

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5.) **(65 points total)** We're going to test the effects of CO gas on cells. Our experiment utilizes a thin, two-dimensional gas of the diatomic molecule CO in a petri dish that has dimensions $a \times b$.

5a.) (5 points) Write down an expression for the full partition function for the CO molecule in terms of constants (include all degrees of freedom).

$$q = \underbrace{q_{trans}}_{\frac{2\pi mkT}{h^2}ab} \cdot \overbrace{q_{rot}}^{\frac{8\pi^2 IkT}{\sigma h^2}} \cdot \underbrace{q_{vib}}_{\frac{e^{-h\nu/2kT}}{1-e^{-h\nu/kT}}} \cdot \overbrace{q_{elec}}^{(g_0 + g_1 e^{-\Delta\varepsilon_1/kT} + \cdots)}$$

5b.) (10 points) Calculate a value for the q_{trans} using T = 37C, a = b = 3cm. Use the mass values of m_O = 16 g/mol and m_C = 12 g/mol.

310 K

$$m_{total} = 28\,g/mol = 4.65 \cdot 10^{-26}\,kg/CO$$

$$q_{trans} = \frac{2\pi mkT}{h^2}ab = \frac{2\pi(4.65\cdot10^{-26}\,kg)(1.38\cdot10^{-23}\,J\cdot K^{-1})(310\,K)}{(6.626\cdot10^{-34}\,J\cdot s)^2}(0.03)^2$$

$$= \underline{\underline{2.56 \cdot 10^{+18}}}$$

5c.) (10 points) What is the U per molecule (U/N)?

$$U = \underbrace{2 \times \frac{1}{2}kT}_{trans} + \underbrace{\frac{1}{2}kT}_{rot} + \underbrace{kT}_{vib} = \frac{5}{2}kT$$

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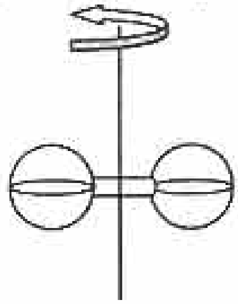
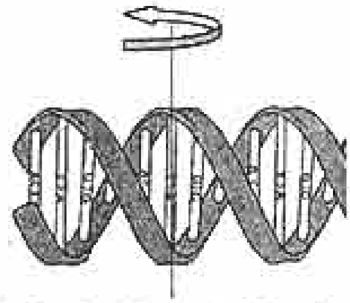
5d.) (10 points) Now let's compare the rotational properties of CO with that of a DNA oligo.





Experimentally you find that the first four energy levels for the diatomic CO to be the following energies:

0J
7.64×10^{-23} J
2.29×10^{-22} J
4.58×10^{-22} J

Determine the bond length for the molecule.

For rotation $\varepsilon_\ell = \frac{\ell(\ell+1)h^2}{8\pi^2 I}$ $\quad I = \mu R^2$ $\quad \mu = \frac{m_1 m_2}{m_1+m_2} = \frac{12\cdot16}{12+16}$ g/mol $= 6.857$ g/mol $= 1.13868\cdot10^{-26}$ kg

$$\varepsilon_1 = \frac{2h^2}{8\pi^2 I} = \frac{2h^2}{8\pi^2 \mu R^2} = 7.64\cdot10^{-23}\,\text{J}$$

$$R^2 = \frac{h^2}{4\pi^2(1.1387\cdot10^{-26}\,\text{kg})(7.64\cdot10^{-23}\,\text{J})} = 1.2783\cdot10^{-20}\,\text{m}^2 \Rightarrow \boxed{R = 1.13\,\text{Å}}$$

5e.) (10 points) Calculate a value for q_{rot} using T = 37°C. What is the rotational temperature for CO?

$$q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = \left(\frac{8\pi^2 I}{2h^2}\right)\frac{2kT}{\sigma} = \frac{2kT}{\sigma\varepsilon_1} = \frac{2(1.38\cdot10^{-23}\,\text{J}\cdot\text{K}^{-1})(310\,\text{K})}{(1)(7.64\cdot10^{-23}\,\text{J})}$$

$$= 111.989 \Rightarrow \boxed{112 = q_{rot}}$$

$$\theta_{rot} = \frac{T}{\sigma q_{rot}} = \frac{T}{\sigma}\cdot\frac{\sigma h^2}{8\pi^2 IkT} = \frac{h^2}{8\pi^2 Ik} = \frac{\varepsilon_1}{2k} = \frac{7.64\cdot10^{-23}\,\text{J}}{2(1.38\cdot10^{-23}\,\text{J}\cdot\text{K}^{-1})}$$

$$\boxed{\theta_{rot} = 2.768\,\text{K}}$$

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5f.) (5 points) If we were make the same measurements in e) at a different temperature, what would happen to the values of the energies observed?)

Same.

5g.) (10 points) Now let's look at the DNA molecule. The oligo is 12 nucleotides long, and each strand has a molecular weight of 3832 g/mol. Calculate the energy levels of the first four rotational states for the DNA oligo. Assume the length is 3.4 Å per base pair. Also assume it is a rigid rod with rotation around the center as shown in the figure, so that $I = 1/12\ ML^2$, where L is the entire length of the molecule.

If $M = 3832\ g/mol = 6.363 \cdot 10^{-24}\ kg/DNA$

$M = 7664\ g/mol = 1.2727 \cdot 10^{-23}\ kg/DNA$

$L = 3.4\ \text{Å} \times 12 = 40.8\ \text{Å} = 4.08 \cdot 10^{-9}\ m$

$I = \frac{1}{12} ML^2 = \frac{1}{12}(6.363 \cdot 10^{-24})(4.08 \cdot 10^{-9})^2 = 8.8268 \cdot 10^{-42}\ kg\ m^{-2}$ or $1.7654 \cdot 10^{-41}\ kg\ m^{-2}$

$$\varepsilon_{rot} = \frac{\ell(\ell+1)h^2}{8\pi^2 I}$$

$$\varepsilon' = \frac{h^2}{8\pi^2 I} = 6.2996 \cdot 10^{-28} \text{ or } 3.1498 \cdot 10^{-28}$$

$$\begin{cases} \varepsilon_0 = 0\ J \\ \varepsilon_1 = 2\varepsilon' = 1.26 \cdot 10^{-27}\ J \text{ or } 6.30 \cdot 10^{-28}\ J \\ \varepsilon_2 = 6\varepsilon' = 3.78 \cdot 10^{-27}\ J \text{ or } 1.89 \cdot 10^{-27}\ J \\ \varepsilon_3 = 12\varepsilon' = 7.66 \cdot 10^{-27}\ J \text{ or } 3.78 \cdot 10^{-27}\ J \end{cases}$$

5h.) (5 points) Calculate the rotational temperature, θ_{rot}, for this rotating DNA oligo. How does this compare to the θ_{rot} for CO?

$$\theta_{rot,DNA} = \frac{\varepsilon'}{k} = 4.565 \cdot 10^{-5}\ K \text{ or } 2.282 \cdot 10^{-5}\ K$$

Much smaller than $\theta_{rot,CO}$

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6.) **(30 points total)** Solutions and Mixtures.

6a.) (10 points) Pure liquid hexane is suspended in a sealed container in the absence of gravity (ok, slightly fictitious! This situation does model a real situation mentioned at the end). The temperature is constant. The hexane does not touch any of the surfaces of the container and is literally suspended in space. Think back to our discussion of surface tension and the free energy associated with creating surfaces of condensed phases. At equilibrium, what geometry (i.e., shape) is the liquid hexane and why?

Spherical, in order to minimize surface area (& total free energy of system). Note that it is possible, depending on how the liquid is added, for multiple little drops to be present. This configuration is a kinetically-determined state, as the drops would fuse upon encountering each other, ultimately creating one large spherical drop.

6b.) (10 points) The hexane in part a is mixed with water and the mixture is suspended in the sealed container in a gravity-free environment, just as in part a. As you probably already intuitively know, $w_{A-A} >>> w_{BB} > w_{AB}$ where A refers to water and B to hexane, and w refers to the bond energy (in fact, a negative number. We are following the convention of the text here to indicate that the A-A bonds are stronger, i.e., a bigger negative number). Sketch the equilibrium configuration of the system, presuming the liquids do not contact any of the container surfaces and are literally suspended in space. Where is the water relative to the hexane, and what geometry (shape) does the liquid have? You may assume that there are comparable total volumes of water and hexane present. (A range of answers was acceptable for this)

The molecules will not be intermixed A-B, due to A A and BB interactions both being stronger than A-B interactions. The molecules would only be intermixed for χ values (p. 271, eq 15.11) < 0 i.e., $w_{AB} > \frac{1}{2}(w_{AA} + w_{BB})$ (keeping in mind the always annoying fact that w's are negative). For $\chi > 0$, 2 situations are possible:

$w_{AB} \geq w_{BB}$

$w_{AB} < w_{BB}$, hexane spreads some on drop of H_2O but depending on magnitude, may separate completely to form another drop:

Credit given for both & anything in between.

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6c.) (10 points) You were not told anything about the relative volume of liquid to the total volume. If the container is sealed after introduction of the liquids, and held at constant temperature, are there any restrictions on how much liquid is added initially so that liquid is present when equilibrium is reached?

Vapor-liquid equilibria dictates that some of the liquid will evaporate in the sealed container. This may result in complete evaporation of the drop if its initial mass is small relative to the mass needed to fill the volume with the appropriate amount of vapor for the specified temp.

Relation to real problems: Malcolm Steinberg, a developmental biologist at Princeton University, proposed that some forces controlling development of multicelluar organisms are analogous to those described in part b. He in fact showed that when two cell types that express the same cell-cell adhesion receptor are mixed in suspension, they behave pretty much the same as the liquids described in part b if cell type A has a lot more of the receptors than cell type B.

For more details, see any book on surface chemistry or for analysis having to do w cell sorting, see Malcolm Steinberg (Science vol 141, pp. 401-408, 1963) & later papers by Foti & Steinberg.

That's it--you're done! Have a great summer!!!