Problem 1:

Assume a system is at constant temperature T, volume V and number of particles N. Determine the relationship between the heat capacity C_V and the energy fluctuations $<(E - <E>)^2>$. You may remember from the first part of the course that C_V is the temperature derivative of the internal energy.

$$\langle (E - \langle E \rangle)^2 \rangle = \overline{E^2} - \overline{E}^2$$

Canonical Partition Fn $\quad Q = \sum_i e^{-\beta E_i}$

$$\overline{E} = \sum_i E_i e^{-\beta E_i} = -\frac{Q'}{Q}, \qquad Q' = \frac{\partial Q}{\partial \beta}\Big|_V$$

$$\frac{\partial \overline{E}}{\partial \beta} = -\frac{Q''}{Q} + \left(\frac{Q'}{Q}\right)^2$$

But $Q''/Q = \overline{E^2}, \quad \frac{Q'}{Q} = -\overline{E}$ $\left(\text{Note } \overline{E} = \langle E \rangle\right.$

or $\frac{\partial \overline{E}}{\partial \beta} = -\overline{E^2} + \overline{E}^2$

and $\frac{\partial \overline{E}}{\partial \beta} = -k_B T^2 \frac{\partial \overline{E}}{\partial T} = -k_B T^2 C_V$

or $\langle (E - \overline{E})^2 \rangle = k_B T^2 C_V$

Problem 2

Consider a system of N independent particles with N very large. Each particle has only two energy levels, 0 and ε.

a) Find the number of microstates, Ω_M, with total energy $E = M\varepsilon$.

b) By using Stirling's approximation, derive the entropy per particle for this system as function of the fraction of particles, x_ε, that are in the highest energy state. Sketch the entropy and mark important points (maxima, minima, etc.) on the x_ε axis (i.e. at what value of x_ε do they occur ?).

c) Calculate the temperature as function of x_ε Discuss the result.

a) $\Omega_M = N! / [M! (N - M!)]$
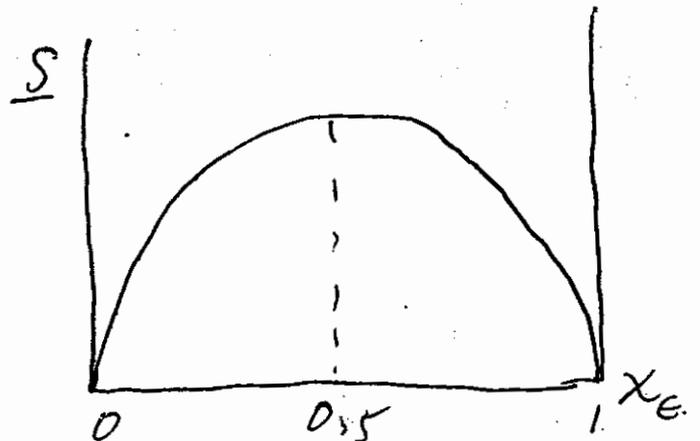
b) $S = k_B \ln \Omega_M = k_B [\ln N! - \ln M! - \ln (N - M)!]$

$S = k_B [N \ln N - N - M \ln M + M - (N-M) \ln (N-M) + (N-M)]$

$S \doteq -k_B N \left[\frac{M}{N} \ln \frac{M}{N} + \frac{N-M}{N} \ln \left(\frac{N-M}{N} \right) \right]$

$\frac{S}{N} = \underline{S} = -k_B [x_\varepsilon \ln x_\varepsilon + (1-x_\varepsilon) \ln (1-x_\varepsilon)]$

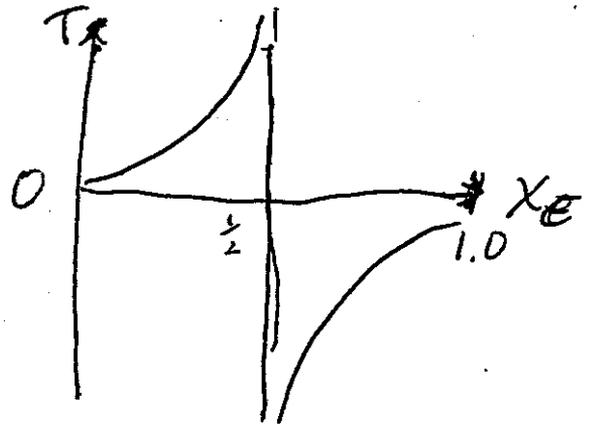max at $x_\varepsilon = \frac{1}{2}$

min at $x_\varepsilon = 0, 1$

c) $\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S/N}{\epsilon \partial X_\epsilon}$

$\therefore \frac{1}{T} = \frac{k_B}{\epsilon} \ln\left(\frac{1-X_\epsilon}{X_\epsilon}\right)$

note: negative temperature
for $X_\epsilon > \frac{1}{2}$ indicating more
particles in upper energy
level than in lower level — LASER type situation.
For Statistical Thermo — consider part only for $T > 0$.

Note: One could also do part c by noting

that $P_\epsilon = \frac{e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}} = X_\epsilon$

or $X_\epsilon = \frac{1}{1+e^{\beta\epsilon}}$

$X_\epsilon(1+e^{\beta\epsilon}) = 1$

$\beta\epsilon = \ln\left(\frac{1}{X_\epsilon} - 1\right)$

$\frac{1}{T} = \frac{k_B}{\epsilon} \ln\left(\frac{1-X_\epsilon}{X_\epsilon}\right)$ as before

Problem 3

Consider a solution of A and B molecules.
If I choose to write the number of ways one can arrange the A and B molecules on a

model lattice by the formula $\Omega_N = \dfrac{N!}{N_s! \, N_p!}$ where N is the total number of molecules

($N_A + N_B$), and express the entropy of mixing as $\Delta S_{mix} = k_B \ln(\Omega_N)$,

a) What assumptions have I made for the configurational entropy of mixing ? Discuss.

b) If A is a solvent and B is a polymer with n segments, is the above formula still valid ?
Discuss. How would you improve it ? Discuss. No equations necessary.

c) Are there other contributions to the entropy of mixing ? Discuss. No equations
necessary.

a) Assumptions

1) No interactions between molecules
   (random mixing = ideal solution)

2) No vacancies, defects, etc.

b) No - EAch of the segments of polymer
are connected - not all configurations possible
in model lattice. Only nearest neighbor sites
of given segment available to neighbouring segment,
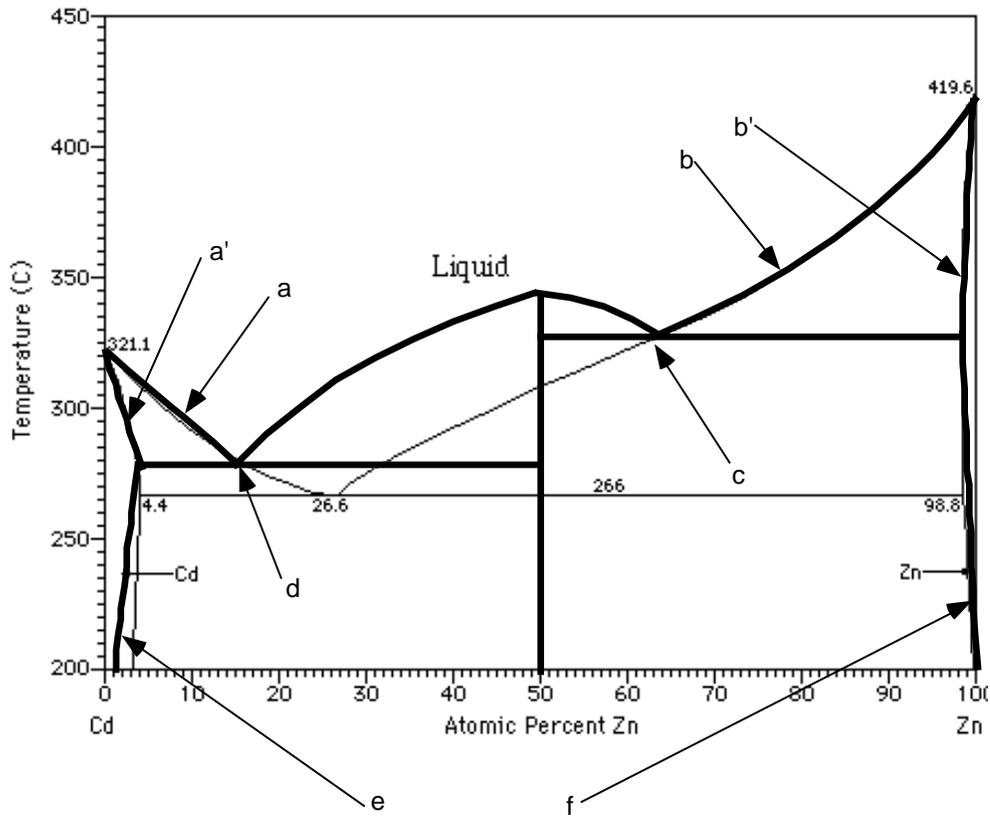etc. as done in Flory Hugains model.

c) Yes.
   Vibrational Entropy - This can be quite large

   Electronic   ''

   Magnetic   ''

Problem 4:

The compound is drawn as a line compound for simplicity, though a compound with off-stoichiometry can also be drawn. Some particular features to look for:

lines a, a', b, b': These represent the two-phase equilibria between the liquid and either the Cd or Zn phase. <u>Nothing is changed to these equilibria as one introduces the compound.</u> This can be easily seen by drawing the free energy curves for the system, with and without the compound.
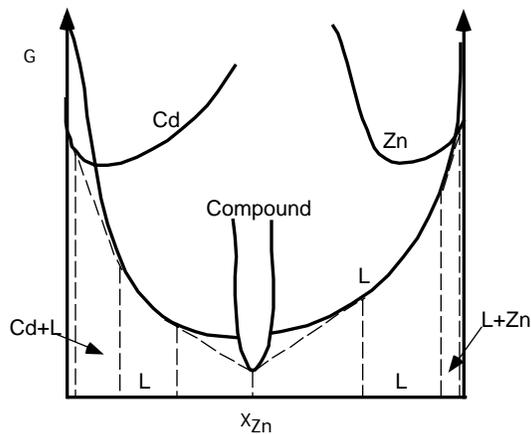
lines e and f: When a new stable appears the solubility limits in the adjoining phases decrease. Again, draw free energy curves to see this.

points c and d: The eutectics are formed when the Cd+L (or Zn+L) two-phase region meets the Li+compound two-phase region.

Problem 5:

Researchers at MIT are working hard to understand the possible phases of the element Donorium (Do) a recently discovered element which is important because it enhances the properties of Endowium (En) when alloyed with it.

Below, the zero-temperature enthalpy and the Einstein temperature (at 1atm pressure) are given for three crystal structures, speculated to be stable for pure Donorium. Donorium is not magnetic at any temperature.

phase	enthalpy at zero K	Einstein temperature
α	0 J/mole	350K
β	5 kJ/mole	475K
γ	7 kJ/mole	200K

What is the stable state at zero K ? Speculate on the possible phase transitions of Do as function of temperature at constant 1atm pressure. **Justify** your answer (possibly with sketches of free energies) and **explain** why each phase transition occurs. There is no need to perform numerical calculations.

Einstein temperature determines magnitude of vibrational entropy. Large Θ_E → stiff material → low S_{vib}. Since we have $G(T=0)$ ($=\Delta H$) and S for each phase $\left(S = -\left(\frac{\partial G}{\partial T}\right)_P\right)$ we know the relative shape of the free energy curves

α most stable at low T since H is lowest

β never becomes stable since entropy is lower than for α

$S_\gamma > S_\alpha > S_\beta$

$T_{\alpha \rightarrow \gamma}$.