

## A lattice model for the phase behavior of two liquids or gasses, A and B.

We can consider mixing of two molecular or atomic species subject to thermal equilibrium of identical size and with some average enthalpic interaction,  $\langle \Delta E \rangle$ . The two species exist, for convenience, on a lattice with N sites of which  $n_A$  are A molecules or atoms. For each species the entropy of mixing can be calculated using the Boltzmann formula,

$$\Delta S_A = -k n_A \ln \phi_A \quad (1)$$

The entropy of mixing for a system of N atoms or molecules

$$\frac{\Delta S}{N} = -k(\phi_A \ln \phi_A + (1 - \phi_A) \ln(1 - \phi_A)) \quad (2)$$

The enthalpy of mixing is related to the average enthalpic interaction through the interaction parameter,  $\chi$ , so the free energy of mixing can be given by the sum of the entropic and enthalpic components,

$$\frac{\Delta G}{NkT} = \phi_A \ln \phi_A + (1 - \phi_A) \ln(1 - \phi_A) + \phi_A (1 - \phi_A) \chi \quad (3)$$

where,

$$\chi = z \langle \Delta E \rangle / kT \quad (4)$$

Figure 1 shows the behavior of equation (3) as a function of volume fraction for various values of the interaction parameter. For low values of interaction parameter the first two terms in equation (3) dominate and the free energy change on mixing is always negative with an upward curvature. This indicates a single-phase regime since fluctuations from a given concentration of equal magnitude in left an right directions always lead to an increase in the net free energy of mixing for the two phases compared to the original single phase. At an interaction parameter of about 2.5 two minima occur in the free energy change curves. These minima indicate two compositions that are in equilibrium since the slope of the free energy curve, or the chemical potential are equal at these two minima. The minima increase in separation as the interaction parameter becomes larger. Since the interaction parameter is proportional to  $1/T$  we have phase separation occurring with decreasing temperature and a gradual spread of the miscibility gap with lower temperature as shown by the phase diagram, temperature versus composition, in Figure 2. The critical point, transition temperature of interaction parameter where the two-phase regime first appears, occurs at an interaction parameter of 2, or at the temperature,

$T_c = z \langle \Delta E \rangle / 2k$ . The critical point in Figure 2 occurs at the peak of the curves.

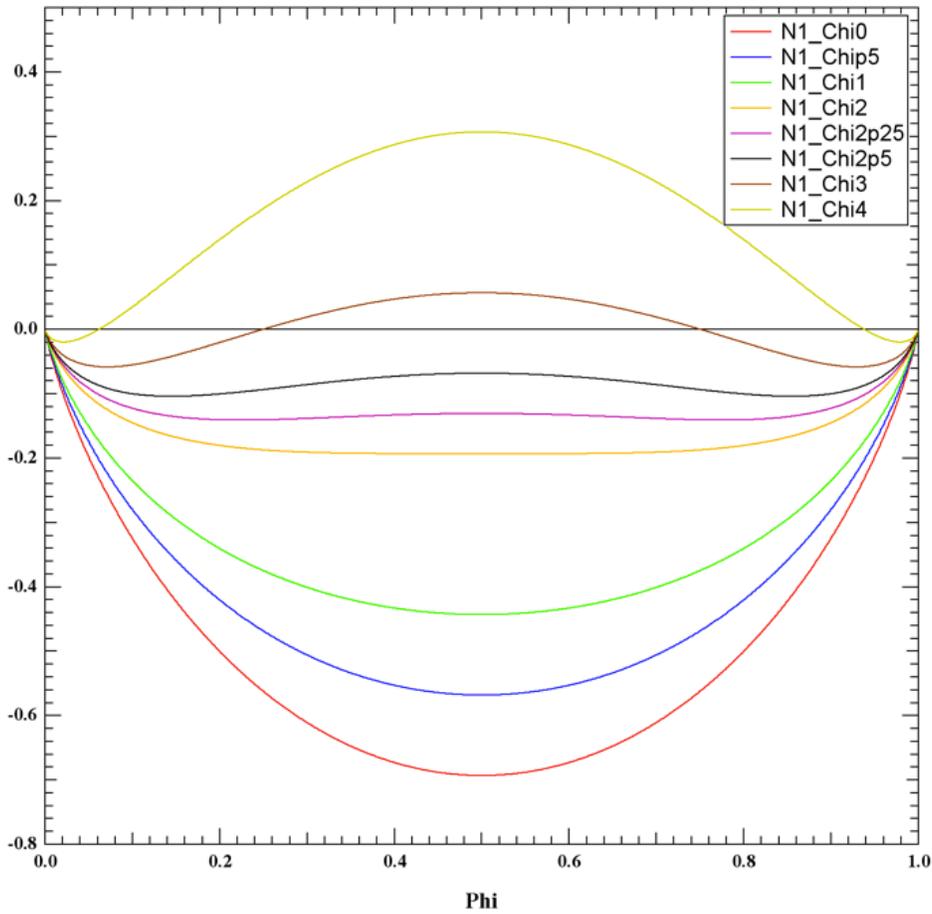


Figure 1.  $\Delta G/NKT$  versus  $\phi$  for equation (4) with  $\chi = 0; 0.5; 1; 2; 2.5; 3$  and  $4$ .

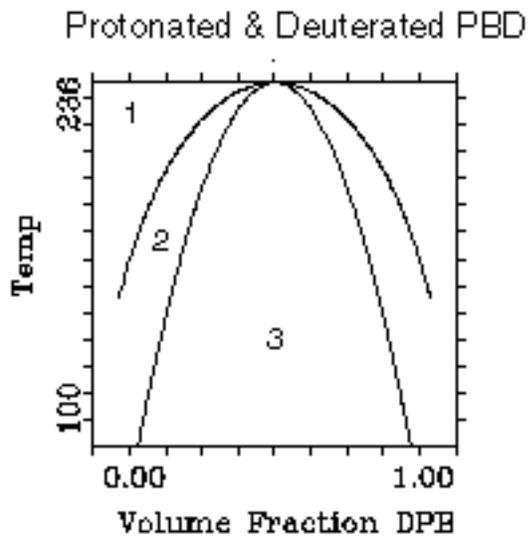


Figure 2. Upper critical solution temperature phase diagram. Regions 2 and 3 are 2-phase regimes, region 1 is the single phase regime. The line between region 2 and 1 is the cloud point curve or the binodal curve.

