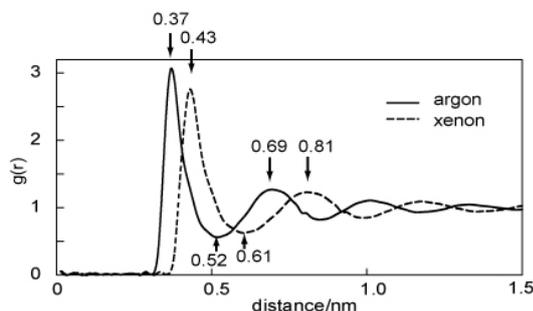


Problems 1

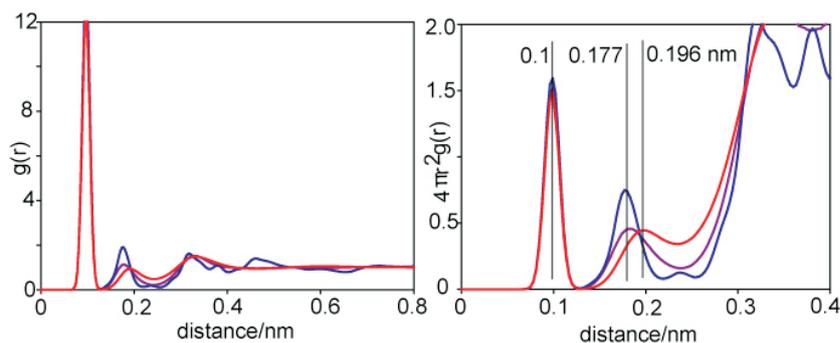
1. (a) Explain what is meant by the pair distribution function of a liquid.
- (b) The pair distribution functions, $g(r)$, for the liquid states of Ar and Xe are shown in the diagram below. Comment on their main features.



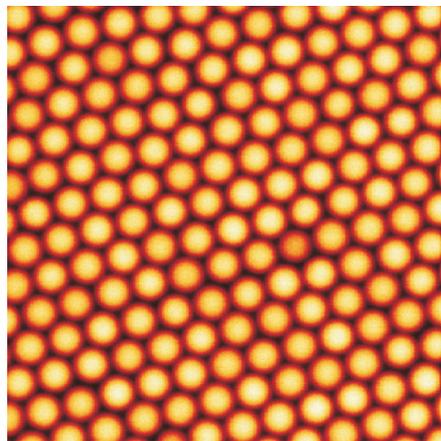
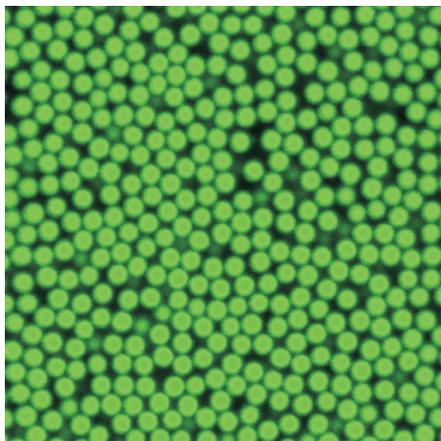
- (c) The energy of interaction, $E(r)$, between a pair of inert gas atoms separated by a distance, r , is given approximately by $E(r) = -\frac{3\alpha'^2 I}{4r^6}$, where the electronic polarizabilities α' (in appropriate units) and ionization potentials I of Ar and Xe are as given in the table below. Calculate the values of E for the two elements at the distance at which they are separated in the liquid.

Inert gas	$I/\text{kJ mol}^{-1}$	α'/nm^3
Ar	1524	$1.6 \cdot 10^{-3}$
Xe	1173	$4.0 \cdot 10^{-3}$

- (d) The energy of vaporization, ΔU , of liquid xenon is 13.3 kJ mol^{-1} . Use the value of E for xenon to estimate the coordination number in liquid xenon.
2. The radial distribution g_{OH} and $4\pi r^2 g_{OH}(r)$ are shown for ice (blue), water at 273 K (purple) and superheated water at 473 K (red) below.



- (a) What is the average hydrogen bond length (O-O distance) in the three situations shown?
- (b) Assuming that each oxygen in ice is hydrogen bonded to exactly four other oxygens, estimate the number of intact hydrogen bonds in water at 273 K and at 473 K, given that the heights of the second peak in the distributions shown on the right above are respectively 0.75, 0.46 and 0.45 for ice, water at 273 K and water at 473 K.
- (c) The enthalpy of fusion of ice is 6 kJ mol^{-1} . Use this value together with your answer from (b) to estimate the average strength of a hydrogen bond (assume that this does not change between ice and water and that the coordination number for water molecules is about 4).
- (d) Use the value from (c) and the mean number of hydrogen bonds per water molecule to estimate how much hydrogen bond energy is lost when water boils. The difference between this value and the observed latent heat of vaporization of water of 40.6 kJ mol^{-1} can be attributed to dispersion forces between water molecules. Using a coordination number of four estimate the mean dispersion force between a pair of water molecules in liquid water.
3. The radial distribution function only depends on the (scalar) distance r . However, the ‘radial’ distribution function can also be constructed in two dimensions: $g(x, y)$, which can be represented as a contour plot. Below, two pictures of two-dimensional colloidal systems are shown, left a colloidal liquid and right a colloidal crystal. Sketch (you don’t have to construct the whole histogram!) the two-dimensional $g(x, y)$ (i.e. the contour plot) and the $g(r)$ corresponding to both images. Discuss the similarities and differences between the $g(r)$ ’s and your sketches for $g(x, y)$. What would the $g(x, y)$ for a two-dimensional cubic crystal look like?



4. The solubility of trinitrotoluene in benzene at different temperatures is:

x	0.279	0.382	0.493	0.622
T/K	303	313	323	333

where x is the mole fraction of trinitrotoluene. Assuming that the solutions are ideal, calculate $\Delta_{fus}H$ and T^* for trinitrotoluene.

5. (a) The Gibbs free energy of an ideal binary mixture is

$$G = G_{\text{unmixed}} + RT \{n_1 \ln x_1 + n_2 \ln x_2\}.$$

Show that the chemical potentials of the components i are (note: $x_1 = 1 - x_2$.)

$$\mu_i = \mu_i^*(T, P) + RT \ln x_i \quad (i = 1, 2).$$

- (b) Show that for an ideal mixture the vapor pressure of each component i is given by Raoult's law

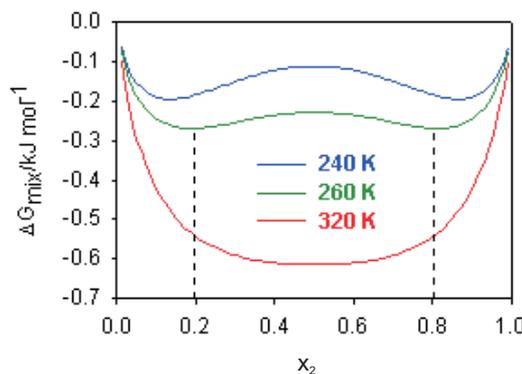
$$P_i = P_i^* x_i \quad (i = 1, 2, \dots)$$

6. (a) Explain what is meant by the term regular solution.
 (b) Write down expressions for the entropy of mixing when two components are mixed to form a regular solution.
 (c) Show how the molar enthalpy of mixing, $\Delta_m H$, in a regular solution of two components, 1 and 2, may be related to the pairwise interactions between its components, w_{11} , w_{22} and w_{12} , via an equation of the form

$$\Delta_m H = w x_1 x_2$$

where w depends on w_{11} , w_{22} and w_{12} .

- (d) The figure below shows a plot of the Gibbs free energy of mixing, $\Delta_m G$, for a two component system, over the full range of molar composition, $x_2 = 0 \rightarrow 1$ and a range of temperatures. Over what range of compositions will the mixture be immiscible when the temperature is 260 K?



(e) The Gibbs free energy per mole as a function of x_2 is given by

$$g \equiv \frac{\Delta_m G}{n_1 + n_2} = wx_1x_2 + RT \{x_1 \ln x_1 + x_2 \ln x_2\}.$$

In the critical point

$$\left(\frac{\partial g}{\partial x_2}\right)_{T_c} = \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T_c} = 0.$$

Show that the critical temperature and composition are given by:

$$\frac{w}{RT_c} = 2, \quad x_{2,c} = \frac{1}{2}.$$

(f) The enthalpy of mixing of an equimolar mixture of acetonitrile and CCl_4 is 1190 J mol^{-1} . Assuming that the mixture obeys regular solution theory, calculate the upper critical solution temperature (UCST).

7. Ethanol is dissolved in an excess amount of water.

(a) Assuming that the mixture behaves like a regular solution, show that the first correction to Raoult's law is given by

$$P_{\text{water}} = P_{\text{water}}^* x_{\text{water}} \left\{ 1 + \frac{w}{RT} x_{\text{ethanol}}^2 \right\}$$

(b) One observes that the total volume of the mixture is smaller than the sum of the original volumes of water and ethanol. Is the partial vapor pressure of water larger, smaller or equal to the one predicted by Raoult's law?

8. The data for the vapor pressure of a mixture of CCl_4 and hexene are given below for a temperature of 40°C . Show that these data are consistent with the regular solution model and determine the interaction (or mixing) parameter w .

x_{CCl_4}	partial vapor pressure CCl_4 (mm Hg)
0.1262	28.88
0.2453	55.20
0.3669	81.35
0.4739	103.80
0.5151	112.00
0.6061	131.24
0.7542	161.86
0.8756	187.06
1.0000	213.34