States of Matter

Physical Chemistry Tutorials

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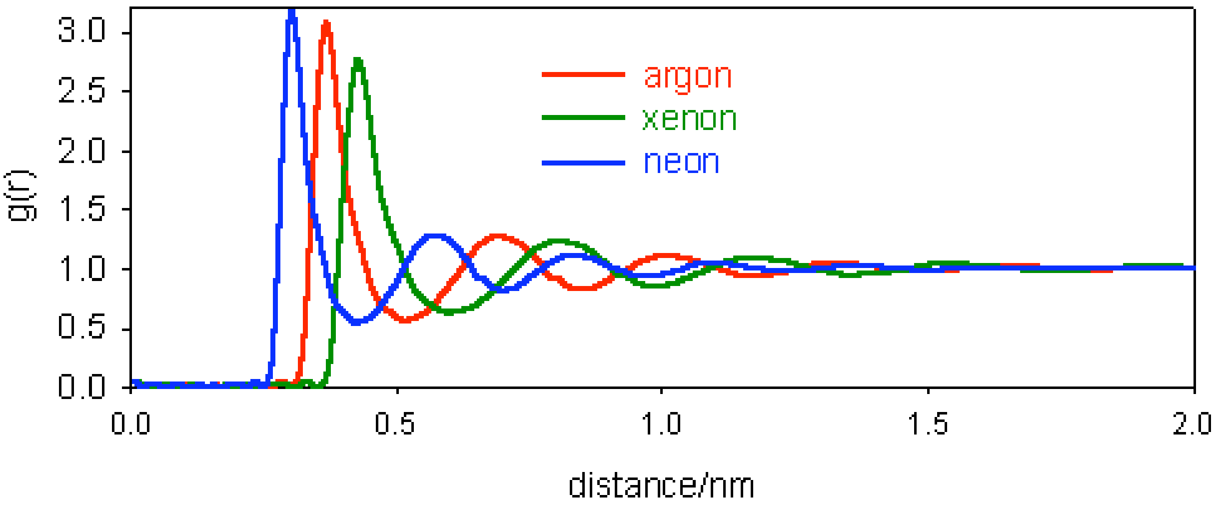
Question 1

The pair distribution functions for the liquid states of Ne, Ar and Xe are shown in the diagram below. Comment on the general pattern of g(r) and estimate the distance between nearest neighbours in each case.



Question 2

Deduce the molecular diameter if NH_3 from each of the following vapour phase viscosity coefficients (a) $\eta = 9.08 \times 10^{-6}$ kg m^{-1} at 270 K and 1.00 bar; (b) $\eta = 1.749 \times 10^{-5}$ kg m^{-1} at 490 K and 10.0 bar. Comment on your results.

Question 3

The Diffusion coefficient for methane in carbon tetrachloride has been measured to have the following values: D = 2.05×10^{-9} m^2 s^{-1} at 0°C and D = 2.89×10^{-9} m^2 s^{-1} at 25°C. Determine (a) the activation energy associated with the diffusion process, (b) the root mean square distance travelled in 1 second in both cases.

Question 4

The mean square displacement in water of latex spheres of radius 0.212 microns is measured to be 128×10^{-12} m^2 in a time of 90s. Use the Stokes equation to estimate the viscosity of water at the temperature of this experiment (25°C).

Question 5

Given that the HCl bond length is 0.13 nm and its dipole moment is 1.8 D, estimate the partial charge on the chlorine atom. (1D = 3.336×10^{-30} C m)

Question 6

Chloroform ($CHCl_3$) is a low boiling liquid. Its molecular weight is 119 and its density 1.48 g cm^{-3}.

a) Estimate the mean separation between molecules in the liquid assuming simple cubic packing.

b) Calculate the dipole-dipole energy, the dipole induced-dipole energy and the dispersion energy between two molecules at this separation at room temperature. ($\alpha' = 8.1 \times 10^{-30}\,m^3$, $I \sim 10^6$ J mol^{-1}, μ = 1D, assume ε=1).

Question 7

The table below lists the electrostatic, induction and dispersion contributions to the intermolecular attractive potential energy for water and ammonia, calculated in each case for an intermediate separation of 0.3 nm. Note that all the energies are in kJ mol^{-1}.

	U_{el}	U_{ind}	U_{disp}
NH_3	-6.2	-0.9	-12.9
H_2O	-16.1	-0.9	-5.3

(a) Use these data to estimate (i) the ratio of the dipole moments and (ii) the ratios of the polarisabilities for ammonia and water. Give an explanation for which molecule has the larger polarisability. (The ionisation potentials of ammonia and water are 10.4 and 12.6 eV respectively).

(b) The quantities given in the table were calculated for 300 K; discuss how these quantities will change with an increase in temperature to 350 K and explain the physical basis of any temperature dependence predicted.

(c) How would the quantities change if calculate for an distance of 0.35 nm?

Question 8

A van der Waals gas obeys the following equation of state;

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Where a and b are constants, assumed to be independent of p, V, and T.

a) Using the identity $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$ show that $\left(\frac{\partial U_m}{\partial V_m}\right)_T = \frac{a}{V_m^2}$ where U_m is the molar internal energy of the gas. Compare this result with that obtained for $\left(\frac{\partial U}{\partial V}\right)_T$ for a perfect gas and comment on this comparison.

b) In the case of helium, the attractive forces are very weak and therefore a~0. (i) Show that by setting a=0 $\left(\frac{\partial(pV_m)}{\partial p}\right)_T$ is independent of temperature for a van der Waals gas.(ii) at 273 K the molar volume of helium at 100 bar is 0.011075 of its molar volume at 1 bar. By assuming the gas behaves as an ideal gas at 1 bar, determine a value for b and hence estimate the diameter of a helium atom.

Question 9

The second virial coefficient B of a gas is related to the intermolecular potential U between two molecules at a distance r by

$$B = 2\pi \int_0^\infty \left[1 - \exp(-\frac{U}{k_B T})\right] r^2 dr$$

Show that for molecules that behave like hard spheres of radius σ (U=∞ when r < σ, U= 0 when r > σ) the virial coefficient is given by $B_0 = \frac{2}{3}\pi\sigma^3$.

Question 10

Trouton's Rule states that $\Delta H_{vap}/T_b \approx$ 85 J K^{-1} mol^{-1}, where ΔH_{vap} is the latent heat of vaporisation and T_b is the normal boiling temperature. The Lennard-Jones well-depth parameter ε is 7.179x4 10^{-21} J for Br_2 and the boiling point is 59°C. Estimate the number of nearest neighbours in liquid Br_2.

Question 11

The Lennard-Jones potential for the interaction of two argon atoms may be written in the form

$$V(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]$$

where r_0 = 342 pm and ε = 1.712 x 10^{-21}J.

a) Sketch the form of this potential and state which of the types of intermolecular force contribute to each term.

b) Derive and expression for the force between two argon atoms at an arbitrary distance r.

c) Calculate the radial position of the minimum in the potential and show that the well depth is equal to ε.

Question 12

The vapour pressure of nitric acid depends on temperature as follows:

T / °C	0	20	40	50	70	80	90	100
P / mmHg	14.4	47.9	133	208	467	670	937	1282

By using a suitable graphical procedure based on the Clausius-Clapeyron Equation, determine (a) the conventional boiling point and (b) the molar enthalpy of vaporization of nitric acid (assume 1 bar = 760 mmHg).

Question 13

Construct the phase diagram for benzene near its triple point (p= 36 mmHg, T = 278.6 K) using the following data.

ΔH_{fus} = 10.6 kJ mol^{-1}

ΔH_{vap} = 30.8 kJ mol^{-1}

ρ(s) = 0.891 g cm^{-3}

ρ(l) = 0.879 g cm^{-3}

Question 14

The enthalpy of fusion of mercury is 2.292 kJ mol^{-1} and its normal freezing point is 234.3 K with a change in molar volume of +0.5178 cm^3 mol^{-1} on melting. At what temperature will the bottom of a column of mercury (density 13.6 g cm^{-3}) of height 10.0 m be expected to freeze?