

Module 2 : Molecular Structure

Lecture 11 : Non-covalent interactions 2 : Structures of Liquids

Objectives

In this Lecture you will learn the following

- Characteristics of the liquid state.
- Radial distribution functions.
- Principles of computer simulations in liquids.
- Time evolution of a simple system using molecular dynamics.

11.1 Introduction

In a dilute gas, the molecules are widely separated and the molecules move several (tens) of angstroms before "colliding" with another molecule. In a liquid, the packing is very similar to that of a solid except that the molecules are moving all the time. In a solid, the molecules are fixed and the spacing between the molecules can be determined by X-ray diffraction. This will be taken up in a later chapter. In a liquid too there is a definite structural arrangement in the vicinity of every particle and when we take an average over the structural arrangement of all the molecules, what we obtain is the structure of a liquid.

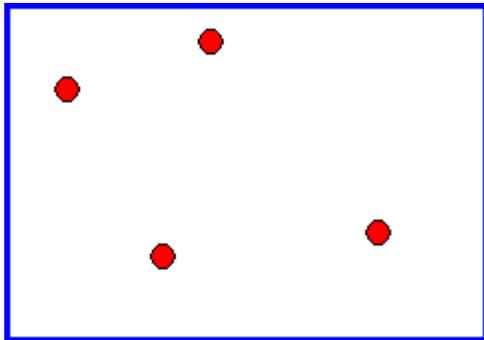
In this lecture, we will characterize this structure and compare it with the structure of solids and gases. The functions characterizing the liquid structure are the spatial distribution functions (similar to the charge densities in atoms and molecules). We will study how these functions are determined by computer simulations. We will consider an explicit time evolution of a three particle system which illustrates the principles of classical molecular dynamics which is used not only in chemistry but also in a number of problems in engineering and molecular biology.

Before proceeding further, an important clarification needs to be made. The structure (of gases, liquids and solids) that is referred to above is not electronic structure, but the relative arrangement of molecules in space. In solids, these molecules are fixed in space and in liquids and gases, they are continuously moving. Electrons however are moving all the time and a "stationary" electron violates the uncertainty principle. The electronic structure of solids (band structure) is considered in a later module.

To describe the electronic structure of liquids, we need to describe the charge densities of moving nuclei. This is at present impractical. The major goal in this lecture is to relate the structure of liquids to intermolecular forces. Before doing so, let us see how the structure of liquids can be quantified.

11.2 Structure of liquids

In Fig 11.1, a small segment of the structure of gases, liquids and solids are shown. The actual box extends to at least a few millimeters. Only a 10^{-20} Å³ section in a plane is shown. We see that in a gas, there are very few molecules separated considerably from one another and there is hardly any "local structure" that has developed.



$$4\pi r^2 \rho g(r) / \text{\AA}^{-1}$$

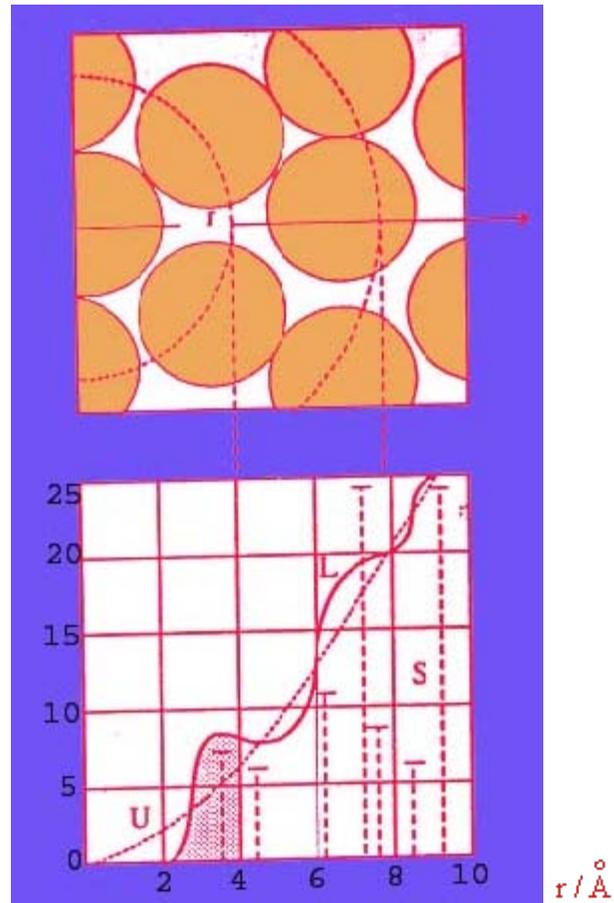


Figure 11.1 A box showing molecules of a gas.

Figure 11.1 (a) The structure of liquid sodium.

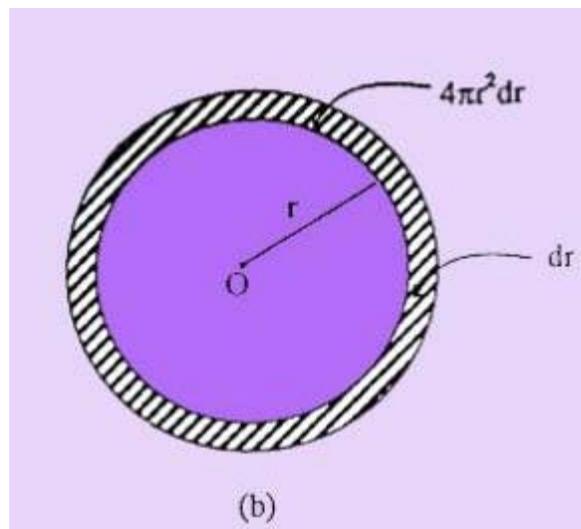


Figure 11.1 (b) A section of a spherical shell of radius r and thickness dr .

The other extreme is the case of a solid where there is "perfect" (in the case of a perfectly crystalline solid at 0 K) order and nothing moves. If we know the position of a single atom /molecule and the lattice spacings in three directions, we can precisely predict the location of all the other atoms in the solid. The case of a liquid is intermediate. Although each molecule is surrounded by other molecules, all are moving. To study an equilibrium property, we can ask questions such as how many nearest neighbours does a molecule have, on the average, and how many second nearest neighbours and so on and then relate the equilibrium property to these average numbers.

A more general query would be how many neighbours are there at a given distance r from a central atom /molecule. To find out this number a spherical shell of radius r and thickness dr is constructed around an atom at the origin. The volume of this shell is $(4/3)\pi(r+dr)^3 - (4/3)\pi r^3$ which is equal to $4\pi r^2 dr$. We count the number of atoms $n(r)$ in this spherical shell. The local density $\rho(r)$ at a distance r from the central atom will then be

$$\rho(r) = n(r) / (4 \pi r^2 dr) \quad (11.1)$$

The bulk (number) density of a liquid ρ is given by N/V where N is the number of atoms in volume V . The unit of this ρ is number/ volume and not g/cc which is used in macroscopic or bulk measurements. We now define the radial distribution $g(r)$ function as

$$g(r) = \langle \rho(r) \rangle / \rho \quad (11.2)$$

where the angular brackets mean that we take the average value of $\rho(r)$. The average is taken over all the molecules and at different times as well. This average value does not depend on any specific atom chosen at the center or any specific instance of time and it is an equilibrium property. A typical sketch of $g(r)$ is shown in Fig 11.2

Figure 11.2 The radial distribution function $g(r)$.

The meaning of this graph can be understood as follows. Most atoms or molecules have a size of about 1 to 3 \AA . If one is considering a distance of 0.1 or 0.5 \AA from the center of an atom, there is no chance of finding an adjacent atom there and hence the local density $\rho(r)$ is zero at very short distances. When one

reaches a value of 3 to 5 \AA , adjacent molecules can be found and the local density when several neighbours are "touching" the central molecule is much higher than the bulk density and hence $g(r)$ is much greater than one.

Between the first set of neighbours and the second set of neighbours there are fewer atoms /molecules and hence $g(r)$ is less than one. The value of $g(r)$ reaches 1 (the asymptotic value) for large distances. At larger r , the influence of the central atom is not significant and hence $\rho(r) = \rho$, the bulk density.

The importance of $g(r)$ stems from the fact that the macroscopic properties of bulk fluids (gases and liquids) can be obtained in terms of $g(r)$. It gives a link between the microscopic structure determined from intermolecular forces and the macroscopic properties such as (thermodynamic) energy (E), entropy (S) and pressure (p). The equation for energy and pressure are given below

$$E / N = 2 \pi \rho \int_0^{\infty} g(r) u(r) r^2 dr \quad (11.3)$$

$$p / \rho k_B T = 1 - (2 \pi \rho / 3 k_B T) \int_0^{\infty} g(r) [du(r)/dr] r^3 dr \quad (11.4)$$

Here E / N is the energy per particle resulting from intermolecular forces. On adding kinetic energy to it, we get the energy used in the first law of thermodynamics. The Boltzmann constant $k_B = 1.38 \times 10^{-23} \text{ J / K}$, T is the absolute temperature and $U(r)$ is the pair-wise interaction potential between two particles. It is assumed here that the interaction between N molecules $U(1,2,\dots,N)$ is pair-wise additive, i.e.

$$U(1,2,\dots,N) = \sum_{i < j} U_{ij}(r_{ij}) \quad (11.5)$$

11.3 Computer simulation in liquids.

A knowledge of the properties of liquids is essential for doing most of chemistry, chemical engineering and biology. While it is not possible to build the theoretical framework for this purpose here, we will outline the principles used in computer simulations which are being used widely nowadays.

Imagine a beaker containing a few moles of water. The system contains about 10^{24} molecules. No computer's memory can handle so many molecules today. Imagine a tiny segment out of this huge number, say about 200 molecules contained in a cubical box as shown below in fig 11.3

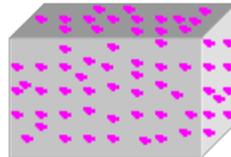


Figure 11.3 (a) About a hundred molecules in a cubical box.

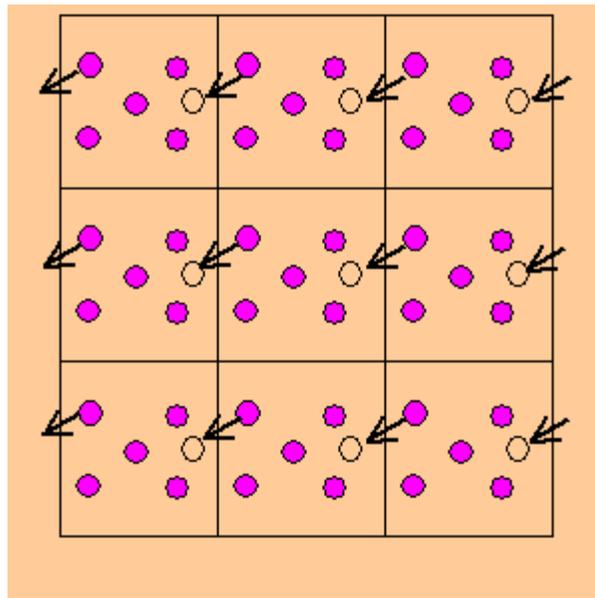


Figure 11.3 (b) A two dimensional box showing periodic boundary conditions.

Imagine the central box in fig 11.3 (a) to be surrounded by identical boxes in the x , y and z directions so as to fill space. The positions of the particles in the central box are arbitrary to begin with and the positions of the particles in other boxes are replicas of the central box. If a molecule moves out of the central box to one side, the corresponding image molecule from the box on the opposite side enters the central box so that the density (number per volume) in the box is unchanged. In this manner, we have generated a bulk fluid [of course it differs from the actual liquid because of the periodicity of fig 11.3 (b)]; but the results of the simulations indicate that a fairly accurate description of fluids is obtained by these techniques.

The major task that remains is to generate the motion of these molecules (as in the real liquid) by using suitable algorithms and then obtain appropriate distribution functions and from these, get the macroscopic properties of the liquid.

11.4 The Monte Carlo (MC) Method

One of the methods for obtaining the bulk equilibrium properties from intermolecular forces is known as the Monte Carlo method. In this method, the initial configuration (set of coordinates of all the N molecules in the box of volume L^3) is chosen and the total energy of the system is calculated using eq (11.5). Then each molecule is moved by a small amount (Δx_i , Δy_i and Δz_i). If σ is the size (radius or the extent in one direction) of a molecule, then the maximum Δx_i is about 0.1σ . Now, all the molecules have obtained a new configuration. Let the energy of the old configuration be denoted U_{old} and let U_{new} be the energy of the new configuration. If U_{new} is less than U_{old} , then the new configuration is accepted and the coordinates are written into the hard disc. If the new energy is greater than U_{old} then the ratio f

$$f = e^{-U_{new}/k_B T} / e^{-U_{old}/k_B T} \quad (11.6)$$

is compared with a random number r which lies between 0 and 1. You can generate a few random numbers on your calculator and verify that they lie between 0 and 1. These are called uniform random numbers (because, they span the range between 0 and 1 uniformly) and there are several standard algorithms to generate these. If the value of f is less than r , then the new configuration is rejected and the old one is written to the disc once again. After this, all the molecules in the current configuration are again moved by (Δx_i , Δy_i , Δz_i) and the new f is compared with another random number r' to see whether the move is acceptable. Using this algorithm about 10^5 to 10^6 configuration are generated and written to the disc. This method is called the Metropolis Monte Carlo method. The values of (Δx_i , Δy_i , Δz_i) are chosen such that about half the moves are accepted. If Δx_i are very large, very few moves get accepted and if Δx_i are too small, a very large number of moves get accepted.

The configurations so generated are referred to as the members of a canonical ensemble. For each member or the configuration that is saved, N , V (volume) and T (the temperature) is the same, but of course the coordinates are different. The distribution of energies in the members has been found to obey the standard Boltzmann distribution (wherein the probability of finding a member with energy U is proportional to $\exp(-U/k_B T)$).

You may have noticed that in the above method, velocities are not used nor have we considered time. The Monte Carlo method is useful for calculating the equilibrium properties such as E , p , and so on. E.g., the average energy of the system under consideration can be obtained as

$$\langle E \rangle = (1 / N_E) \sum_i E_i \quad (11.7)$$

Here, E_i s are the energies of the members of the ensemble (N_E) generated by the MC algorithm described above.

11.5 Classical Molecular Dynamics.

In this method, the time evolution of the system of N particles is studied using the classical (Newtonian) equations of motion ($\vec{F} = m \vec{a}$). Since it is not possible to find the explicit formulae for all the positions $\vec{r}_i(t)$ and velocities $\vec{v}_i(t)$ as a function of time, the equations of motion are integrated using algorithms whose accuracy depends on the discretized time step δt used in the dynamics. In this method, the forces on each particle are calculated at each time step using

$$\vec{F}_i = - \frac{\partial}{\partial \vec{r}_i} \sum_{i < j} u_{ij}(r_{ij}) \quad (11.8)$$

One of the simplest algorithms is the Verlet algorithm.

In this algorithm, the displacement of a particle \vec{r}_i at time $t + \delta t$ is obtained in terms of its displacements at times t and $t - \delta t$ as follows

$$\vec{r}_i(t + \delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \delta t) + \frac{1}{m} F_i \delta t^2 \quad (11.9)$$

$$\vec{v}_i(t) = [\vec{r}_i(t + \delta t) - \vec{r}_i(t - \delta t)] / 2\delta t$$

The velocity of the particle does not play a dynamical role in this algorithm, but its value can be easily obtained from

$$\vec{v}_i(t) = [\vec{r}_i(t + \delta t) - \vec{r}_i(t - \delta t)] / 2\delta t \quad (11.10)$$

In this method, the position and velocities of all the particles are obtained during each step of the simulation and are written to the hard disc. Typically 10^5 to 10^6 configurations are generated in the simulation. In these configurations, N, V and E (energy) of each member is the same.

From the distances between all the pairs of particles in all the members ($r_{ij} = [(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2]^{1/2}$) $g(r)$ can be obtained.

To determine $\vec{r}_i(t + \delta t)$, we need the value of \vec{r}_i at two time steps t and $t - \delta t$. This is fine for all intermediate steps except the first step. In the first step only $\vec{r}_i(0)$ is known. To get $\vec{r}_i(0 + \delta t)$ we may use the well known Newton's formula $s = ut + 1/2 at^2$, i.e.,

$$\vec{r}_i(\delta t) = \vec{r}_i(0) + \vec{v}_i(0) \delta t + 0.5 F_i(0) \delta t^2 / m \quad (11.11)$$

To use eq. (11.11) we need to obtain the velocities $\mathbf{V}_i(0)$ of all the molecule from a Maxwell-Boltzmann distribution of velocities,

$$f(v) dv = 4 \pi (m / 2 \pi k_B T)^{3/2} \exp(-mv^2 / 2k_B T) v^2 dv \quad (11.12)$$

An example of a 3 particle molecular dynamics (MD) is shown in Table 11.2. The initial coordinates are shown in fig 11.4. For simplicity, only the motion in the xy plane is considered.

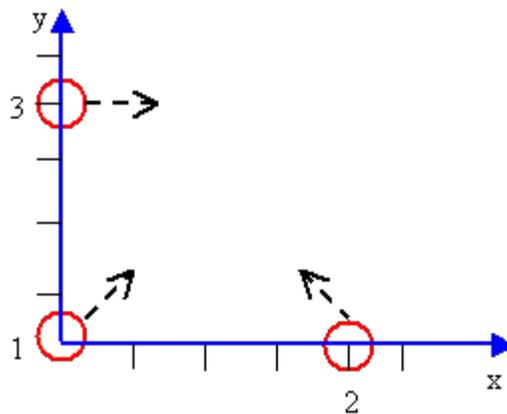


Figure 11.4 Initial configuration of a three particle system.

Table 11.2

Components	Particle No. 1		Particle No.2		Particle No.3	
	x	y	x	y	x	y

Step Number 0						
Forces	55.47	55.47	-68.3	12.8	12.8	-68.3
Positions	0.00	00.00	4.00	0.0	0.0	4.0
Velocities	0.00	0.00	0.00	1.00	1.00	0.00
Step Number 1						
Forces	+55.56	55.56	-68.8	13.23	13.23	-68.08
Positions	0.00174	0.00174	3.9979	0.0504	0.0504	3.9979
Velocities	0.0347	0.0347	-0.0427	1.008	1.008	-0.0427
Step Number 2						
Forces	+54.3	54.3	-68.3	13.98	13.98	-68.3
Positions	0.00695	0.00695	3.9914	0.1016	0.1016	3.9914
Velocities	0.0695	0.0695	-0.0057	0.0163	0.0163	-0.0857
Step Number 3						
Forces	51.4	51.4	-66.5	15.14	15.14	-66.5
Positions	0.0156	0.0156	3.9807	0.154	0.154	3.9807
Velocities	0.1383	0.1383	-0.172	1.0333	1.0333	-0.172

Table 11.2 coordinates of a three particle (Ar) system in the first three steps. The potential used is $4 \epsilon [(\sigma/r)^{12} - (\sigma/r)^6]$ and $\delta t = 0.05$ ps. Initial velocities are (0,0), (0,1) and (1,0) for the x and y components for the three particles. The units are $\text{\AA}/\text{ps}$. The initial positions of the three particles 1,2 and 3 are, in \AA s, (0, 0), (4,0) and (0,4). The mass of Ar is 39.95 g/mol. With these units of mass and velocity, the unit of force becomes $10 \text{ J}/(\text{mol}\text{\AA})$.

11.6 Potential Energy Functions

The form for the potential energy function is central to the success of any computer simulation. The forms are either empirical (determined by fitting to the experimental thermodynamic or kinetic data) or are obtained from the wavefunctions and energies of molecules. In this section we just mention two of the typical forms. If species i and j are spherical with diameters σ and charges q_i and q_j , the interaction energy may be written as

$$U_{ij}(r_{ij}) = 4 \epsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6] + q_i q_j / r_{ij} \quad (11.13)$$

This is the well known Lennard-Jones (LJ) + Coulomb form.

The interaction between two molecules may be calculated if, for example, interaction sites can be placed at various atoms in the molecule. A model for water referred to as the simple charge model places a charge of $-0.82e$ on oxygen and $0.42e$ on the hydrogens. The bond length between O and H is $1 \overset{\circ}{\text{A}}$ and the bond angle is $109^\circ 28'$. This is shown in fig 11.5.

Figure 11.5 The Simple Point Charge model of water.

The interaction between two molecules is the sum of the nine Coulombic interactions (interaction of each charge on one molecule with each of the three charges on the other molecule) plus an additional LJ interaction between the two oxygens given by

$$U_{O-O}^{LJ}(r) = (B/r)^{12} - (A/r)^6 \quad (11.14)$$

The values of A and B are $0.37122 \text{ (kJ/mol)}^{1/6} \text{ nm}$ and $0.3428 \text{ (kJ/mol)}^{1/12} \text{ nm}$, and r is the distance between two oxygens. $1 \text{ nm} = 10^{-9} \text{ m}$. Although the bond angle in this model is higher than the value of the bond angle in the vapour phase and the dipole moment too is different from the vapour phase value of 1.8 D , this model predicts good structure for liquid water. One of the simple message is that the molecular structure and geometry in a liquid gets affected by the presence of the densely packed neighbouring molecules.

The distribution functions $g(r)$, now get extended to $g_{HH}(r)$, $g_{OO}(r)$ and $g_{OH}(r)$. In $g_{OH}(r)$, the oxygen is on one water molecule and H on another water molecule. These distribution functions are shown in fig 11.6

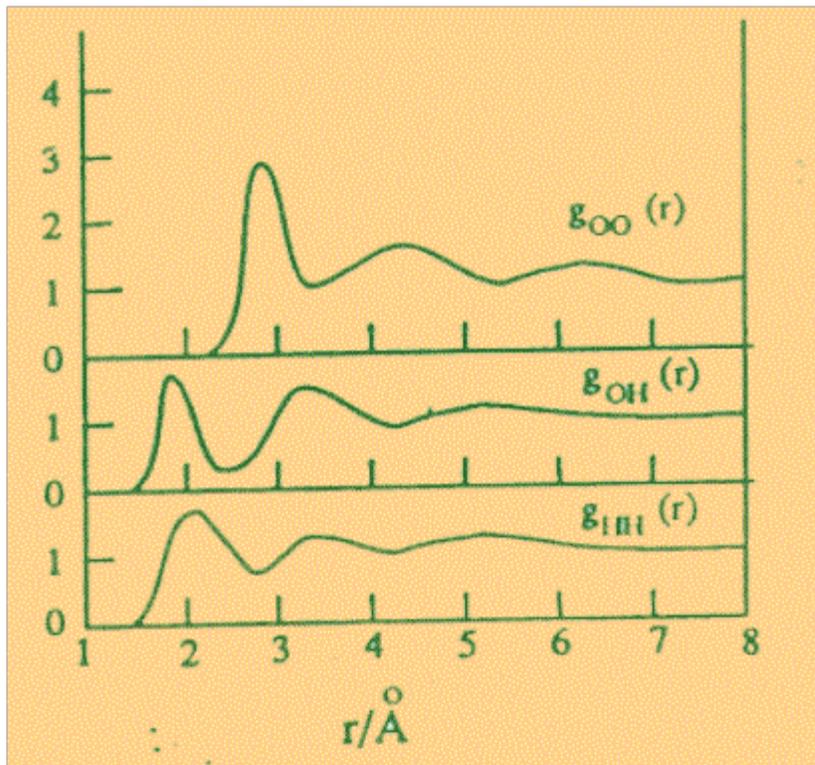


Fig 11.6 The O-O, O-H and H-H pair distribution functions in water.

From these functions we can obtain, among other things, the coordination number around each water molecule, i.e., how many water molecules surround a given water molecule at a distance, say 3 \AA . This is given by

$$\text{coordination number at } 3 \text{ \AA} = 4 \pi \int_0^{3 \text{ \AA}} g(r) r^2 dr \quad (11.15)$$

11.7 Problems

11.1) Calculate the second virial coefficient B_2 , for a system wherein the particles interact via a) a hard sphere potential and b) a square well potential. Evaluate the value of B_2 when $\sigma = 3.4 \text{ \AA}$, $\epsilon / k_B = 120 \text{ K}$ and $\delta = 3.4 \text{ \AA}$

11.2) At what value of r does the Lennard-Jones (LJ) potential have a minimum value of $-\epsilon$?

11.3) Generate a set of about 50 random numbers from your calculator and estimate their average value and the standard deviation from the average.

11.4) Give about three examples of intramolecular and intermolecular hydrogen bonding (other than the examples given in lecture).

11.5) Estimate the effect of dipole moment (μ) on the boiling points (T_b) by comparing u_μ vs T_b for the following sets of molecules

a) CH_3Cl , $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_3\text{H}_7\text{Cl}$

b) o-, m- and p- dichlorobenzenes.

You need to get the data from a handbook of chemistry/physics.

11.6) In one second, what is the (approximate) average distance through which a nitrogen or oxygen molecule moves in air and a water molecule moves in liquid water at room temperature?

11.7) In this lecture, we have discussed the nature and the pair distribution functions. How is the height of the first peak affected by an increase in temperature?

11.8) For two electrons separated by $r = 4 \text{ \AA}$, what is the value of the electrostatic energy? Compare this value with the LJ interaction energy between two Ar atoms at 4 \AA , and also the gravitational energy of attraction between two Ar atoms separated by the same distance.

11.9) Will the product of the quadrupole moment and the diameter (approximate diameter in case of non spherical molecules) of the molecule give the polarizability of the molecule? Justify your answer.

Recap

In this Lecture you have learnt the following

Summary

In this lecture, we have used our knowledge of intermolecular potentials (forces) to investigate the structure and molecular movement in liquids. The radial distribution function $g(r)$ was defined. If a molecule is located at the origin, $g(r)$ gives the ratio of local density $\rho(r)$ at r and the bulk density.

The thermodynamic properties of liquids can be obtained from this and other more detailed distribution functions. Equation (11.3) and (11.4) give the internal energy and pressure. Computer simulation methods are one of the "simplest" means to obtain these distribution functions. The central quantities are the intermolecular forces. The intermolecular forces between two complicated molecules depend on the relative distances and orientations. It is best to represent a molecule as a collection of sites and to estimate the interaction between two molecules as the pairwise sum of the interactions of all sites of one molecule with all the sites of the other.

A three site simple point charge (SPC) model of water was described in this lecture. The O-O, O-H and H-H distributions in liquid water were also presented and simple algorithms to perform Monte Carlo and classical molecular dynamics simulations were outlined.