CHAPTER TWO

COMPUTER SIMULATIONS and PROPERTIES

2.1 Introduction to Computer Simulation

Over the last two decades, modern silicon technology has resulted in the production of faster, larger and more powerful computers. Every year, newer and faster machines appear. At present the trend is going from conventional serial Von Newmann processors to a much faster parallel computers example supercomputer like "CRAY T3E" which can have up to thousand central processing unit. Computations which may have taken several hours in the early sixties now take only a few seconds. This recent dramatic upsurge in computer power has therefore spread beyond the confines of statistical physics to include groups such as physical chemists, solid state physicists, materials scientists and increasingly, biochemists and biophysicists to apply the technique of computer simulation into thier studies.

Before discussing computer simulation in detail however, we must first of all ask, why is the technique of computer simulation so important. From a theoretician's point of view, this technique is extremely valuable in that it provides a tool to perform 'exact experiments ' on well defined model systems thus enabling these "computer experiments" to be compared directly with both real experimental data and predictions from theories. For instance, we can modelled a system of nematic liquid crystals by choosing a particular interaction potential. But in order to obtain properties for the model system, some theory which is always in the form of approximation is needed.

However in computer simulation we can use the same model system and simulate its properties. This provides a mean to test the theory without affecting the validity of of the model. Conventionally the theory is tested by comparing results from real experiments. The disadvantages of this method is when results are not in agreement, there is no way of knowing if both theory and the model are wrong or just one of them. Therefore the best method to test a theory is to use both computer simulation and real experiment, as illustrated in Figure 2.1[24].

The properties of dilute atomic gases can be obtained directly from an analytical solution of a mathematical model, since the system can be regarded as consisting of totally independent entities, for example, particles or oscillators. However for more condensed systems this analytical mathematical approach is not possible, since for compressed gasses or liquids the atoms or molecules interact with each other giving a many bodied, multi-interaction problem. To an extent this problem can be overcome by resorting to the computer simulation techniques, at least for relatively simple systems, where the interaction potential can be regarded as adopting a simple form, and consisting of pairwise interactions only. In the case of the simulation of atomic liquids, for example liquid argon, a high degree of agreement can be obtained between data measured experimentally and that calculated from computer simulations [25,26], thus providing a fairly rigorous test to the derived pair potentials. The same is true, although to a lesser extent, in the simulation of the properties of molecular liquids, such as liquid nitrogen, hydrogen chloride and even for simple triatomic molecules, like carbon disulphide and water [27,28]. However, for more complex molecules, approximations have to be made

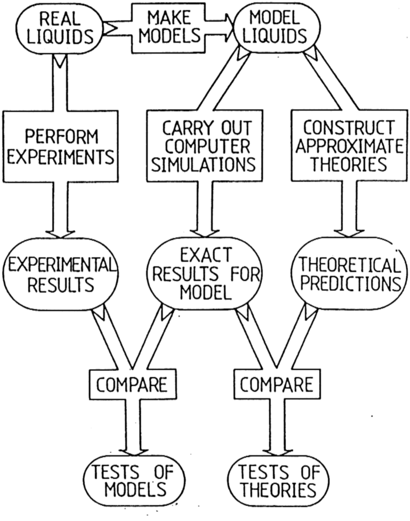

Figure 2.1 The connection between experiment, theory, and computer simulations.

to formulate the pair potential before the simulation can be attempted. For systems consisting of large molecules, it would be computationaly very demanding to account for all interactions and so assumptions related to the symmetry of molecules and to the form of interaction potential have to be enforced. Even so, the simulation of such systems does provide a very important probe into the understanding of the properties of such molecular systems.

In conjunction with the dramatic developments that have occurred in computer technology, the use of simulation has greatly extented the range of problem to which the methods of statistical mechanics can be applied. Although the statistical mechanics of any condensed phase which is complex, but modelling interactions among the liquidlike properties and solid like properties of liquid crystalline systems is possible but nevertheless is a challenging exercise. This is especially true when considering the dependence of liquid crystalline phase transition on the temperature and on the nature of the molecular interactions. As a consequence, it is becoming a more common for researchers to turn to computer simulation to gain better insight into the behaviour of liquid crystals. Many liquid crystals may be considered as assemblages of rodlike molecules that prefer to locally align themselves along a common "director axis ". Nematic liquid crystals, are perhaps the simplest of liquid crystalline system, and are thus the easiest to simulate, this will be discussed in detail later.

Clearly computer simulation allows not only laboratory obtainable data to be calculated such as heat capacity, etc. In addition it can also gives exact results, for example it provides direct route from the microscopic details of a system (the mass of the atoms, the interaction between them, molecular geometry etc.), to macrosopic properties of experimental interest (the equation of state, transport coefficients, structural order). As well as being of academic interest, these type of information can also be technologically useful (e.g polymer-dispersed liquid crystal (PDLC) film whereby it has become the subject of much scientific investigation and commercial development). It may be difficult or impossible to carry out experiments under extremes of temperature and pressure, while a computer simulation of the material such as a shockwave, high temperature plasma, a nuclear reactor, or a planetary core, would be perfectly feasible. Quite subtle details of molecular motion and structure, for example in heterogeneous catalysis, fast ion conduction, or enzyme action, are difficult to probe experimentally, but can be extracted readily from a computer simulation. Finally, while the speed of molecular events is itself an experimental difficulty, it present no hindrance to the simulator.

2.1.1 Periodic Boundary Condition

There are two technique involved almost universally in computer simulation, the Monte -Carlo technique, and the method of Molecular Dynamics. Before describing in details of the two technique, we shall look at some problems associated with both techniques.

Firstly and perhaps the biggest problem is associated with the size of the systems studied. Computer simulations are usually performed on a small number of molecules, typically from a few hundred to a few thousand in the most favourable cases. The size of the system is limited by the available storage on the host computer and also the speed of execution of the program. Several hundred particles does seem a small number indeed when compared to the number, of the order of 10^{23}, present in a macroscpic system or with those of real experiments. Indeed early computer simulation studies used as few as 32 molecules [29] and even today, few simulations are performed on systems with more than 1000 interacting atoms or molecules (particles). This therefore means that in order to predicts the properties of essentially infinite systems from our small finite system, a careful extrapolation has to be performed. However, bulk properties are only weakly dependent on N, where N is the number of particles, for N greater than 100 [30] except for properties calculated close to a phase transition, where, statistically a true phase transition cannot occur except in infinite systems.

The fact that small systems have to be used, gives rise to a further problem, that of surface effects. Clearly for a system of 1000 particles a relatively high proportion will exist at or close to a surface, which, will produce adverse properties. To remove these surface abnormalities, Metropolis et al, 1953; [31] introduced the so-called "perodic boundary conditions". This involves surrounding the isolated system of N particles by an infinite number of exact replicas of itself. Thus a particle at a position (x, y, z) in the cell will see exact replicas of itself at positions $(x \pm n_a a, y \pm n_b b, z \pm n_c c)$, where (n_a, n_b, n_c) each adopt all integer values between 0 and ∞, and in this case the cell is defined to be rectangular with dimensions (a, b, c). Also, when a particle is moved out through one face of the cell it automatically reenters at the opposite face in order to preserve N. This effect is depicted in Figure 2.2 for a two dimensional square system. In general any

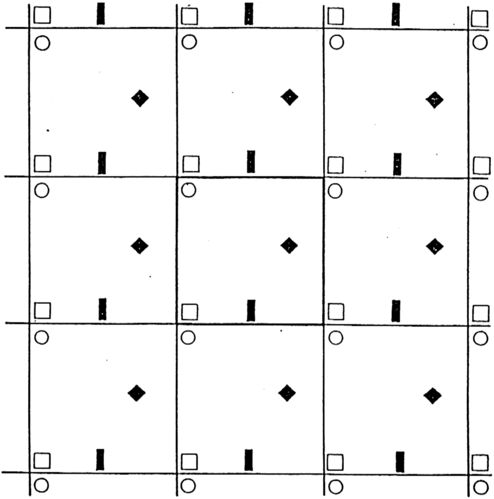

Figure 2.2 Two dimensional periodic boundary conditions.

shaped cell can be used provided that on replication it fills all space. Thus in two dimensions the cell could either be triangular, square, rectangular or hexagonal. In three dimensions it is usual to use a cubic cell giving cubic periodic boundary conditions, although other more complex cells have been used, for example, truncated octahedra [32]. Recently a new alternative to common periodic boundary condition is proposed, called "Nebula Boundary Condition" (NBC)[33]. The basic idea of the NBC method is to sample the molecules close to the centre of the sphere more often than those close to the surface. This preferential sampling method would therefore reduce enormous computational requirements.

The major disadvantage with periodic boundary conditions is that it introduces spurious periodic correlations with a regularity equal to cell dimensions, therefore in calculating distance dependent correlation and distribution functions one must always be aware of this effect.

Another problem encountered in computer simulations, although not as severe as the difficulty encountered using a finite number of particles, is the choice of a starting configuration, which define the positions and orientations of the N particles in the cell at the start of the calculation. Generally at a specific set of external conditions (for example, temperature, pressure) the system will exist in its equilibrium state, therefore unless the starting configuration for a specific simulation is an equilibrated one, a stage during which the system allowed to equilibrate will have to be undertaken. This equilibrium process can be minimised with judicious choice of starting configuration, since it is unlikely that a fully equilibrated stste will always exist. For example, at low temperatures it is sensible to take a configuration representative of the degree of order which would exist at low temperatures, in other words an ordered state, and similarly at high temperatures where a totally random state would represent the high degree of disorder present.

2.2 Simulation Technique

There are wide range of simulation techniques, from straight forward solution of Newton's equations of motion; *Molecular Dynamics*, to more specialised stastistical mechanical sampling methods , usually termed *Monte-Carlo.* Thier common feature is the fact that they are based on a molecular description of the system of interest; the main part in each case is the law that describes the interactions between the constituent particles, whether they are atoms, molecules or ions. The different versions of the Monte -Carlo method are schemes for sampling from a probability distribution appropriate to one of the ensembles of equilibrium statistical mechanics. In the Molecular Dynamics, the particles are allocated initial coordinates and momenta, and thier subsequent trajectories are mapped out by integration of the classical equations of motion. Observable properties of the system are then obtained as time averages over the trajectories. Hence Molecular Dynamics, at least in its conventional form, represents a realization of Boltzmann's approach to statistical mechanics, whereas the Monte -Carlo method is rooted in Gibbs formulation of the problem. Molecular Dynamics can be used in the study of time -dependent process. However the Monte -Carlo method has its own advantages and is often simple to apply. The result reported in this thesis are all based on Monte-Carlo simulation, so we shall concentrate on this techniques further.

2.3 The Monte -Carlo Method

The canonical ensemble average of a N-particle system can be written in general as,

$$\langle M \rangle = \int M(X^N)\, P^N(X^N)\, dX^N, \tag{2.1}$$

where $P^N(X^N)$ is the N- particle probability distribution function. A particular example of an average like (2.1) might be the average configurational internal energy of an ensemble of N particles, which can be written as

$$\langle U \rangle = \int U(X^N) P^N(X^N) dX^N, \tag{2.2}$$

X^N denotes the N configurational variables X_1, X_2,............., X_N, where X_i represent the variable in space and orientation (X_i, Y_i, Z_i, α_i, β_i, γ_i). dX^N represent dot product where $dX_1 . dX_2 . dX_3$..........dX_N is a function of all the coordinates of N particles, where

$$P^N(X^N) = \frac{\exp(-U(X^N)/kT}{Q_N},$$

Q is the partition function, with,

$$Q_N = \int \exp(-U(X^N)/kT)(dX^N),$$

$U(X^N)$ will typically be the sum of potential energies between pairs of particles although, of course, many -body forces or external forces can be included. However it is usually approximated to be sum of pairs potential,

$$U(X^N) = \sum_{i \neq j} U_{ij}(X_i X_j).$$

The intergral in eq (2.2) can be replace by a sum ,

$$\langle U \rangle = \lim_{M \to \infty} \sum_{i-1}^{M} U_i(X^N) P_i^N(X^N), \tag{2.3}$$

where $U_i(X^N)$ is the potential energy of the configuration denoted by the symbol i and M is the total number of configurations, in a set , say S, for N particles in a volume V. Because M is so large it follows that any attempt to compute <U> directly from eq. (2.3) is a hopeless task. On the other hand, by averaging over a smaller number of configurations, m say, we could hope to obtain an estimate for <U> from,

$$\langle U \rangle = \sum_{i=1}^{m} U_i(X^N) P_i^N(X^N), \tag{2.4}$$

The crudest Monte -Carlo method is designed to do precisely this. In practice it does not work because any randomly selected configuration is likely to be a highly improbable one, contributing very little to the sum in eq. (2.4).Futhermore estimation of an average <U> in eq. (2.4) is not quite correct, because the partition function, Q, must be the sum over all state.

It is therefore essential to use some form of " importance sampling " whereby configurations are selected according to a prescribed probability distribution function, and when averaging over the m configurations in the sample, a weight is attached to each which has the effect of eliminating the bias in the selection was mention by Metropolis et al in 1958[31]. A flow chart of the scheme is given in Figure 2.3 overleaf. This amounts to choosing the prescribed probability distribution function equal to the Boltzmann distribution. In this case the average is obtained simply as,

$$\langle U \rangle = m^{-1} \sum_{i=1}^{m} U'_i(X^N), \tag{2.5}$$

where $U_i'(X^N)$ is a weighted sample set.

The answer to the question of how to sample according to the required distribution is best formulated in the language of Markov processes (30,34,35). The problem is that of forming a sample by generating a Markov chain in which the successive states are configurations drawn from set S. Although no physical time is involved, it is useful for descriptive purpose to speak of the states of chain occurring at "times" t , t+1, t+2,.....,etc. From eq. (2.5) we see that the aim is to generate the chain in such a way that the weighted average of U over all states of the chain converges, for sufficiently large m, to the canonical ensemble average <U>. Clearly this equivalence between the two averages will be assured if asymtotically a state i recurs in the chain with a frequency proportional to the Boltzmann factor. For this to be true the one - step

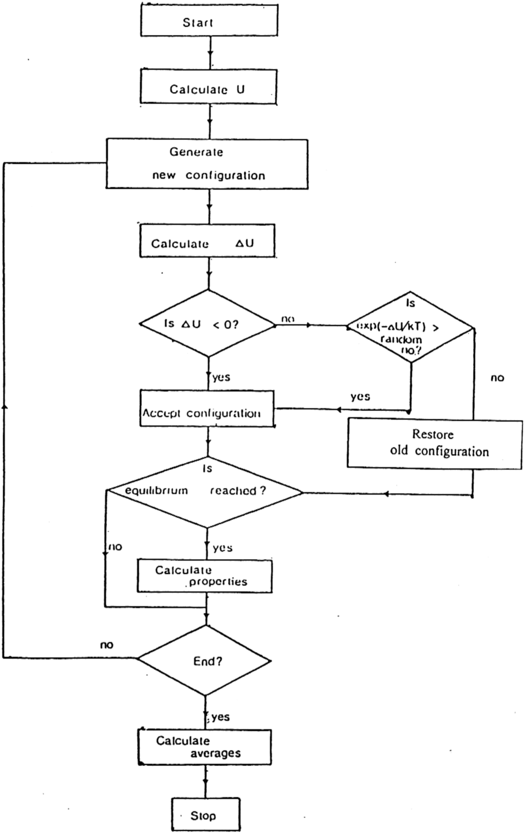

Figure 2.3 A schematic representation of the Monte - Carlo algorithm.

transition probabilities which characterize the Markov process must have the following properties.

2.3.1 The Theory of Markov Chains

Let P_{ij} = P_{ij} [36] be the conditional probability that if the system in the state i at time t will be in the state j at time t+1, P_{ij} is called the one step transition probability. The transition matrix [P_{ij}] is independent of time and its elements must satisfy the conditions,

$$P_{ij} \geq 0, \qquad (2.6)$$

$$\sum_{j=1}^{M} P_{ij} = 1, \qquad (2.7)$$

An n-step transition probability is defined by the recurrence relation,

$$P_{ij}^{(n)} = \sum_{k=1}^{M} P_{ik}^{(n-1)} P_{kj}, \qquad (2.8)$$

It is known that if every state can be reached from any other state with a certain sequency of steps (the system is ergodic) then the limit,

$$\lim_{n \to \infty} P_{ij}^{(n)} = W_j, \qquad (2.9)$$

exists for every pair, i, j and is independent of the starting state i. In addition it is found that the asymptotic frequency factor w_j obey the relations,

$$w_j \rangle 0, \tag{2.10}$$

$$\sum_{j=1} w_j = 1, \tag{2.11}$$

from eqs (2.8) and (2.9)

$$w_j = \sum_k w_k P_{kj}, \tag{2.12}$$

In our case we know that the asymptotic frequency factors should be; if every configuration represents a state of a Markov chain, then we require

$$w_j = \frac{\exp(-U^{(j)}/kT)}{Z_N}, \tag{2.13}$$

where $U^{(j)}$ is the energy of the j th configuration. Eq.(2.10) and (2.11) are automatically satisfied by this choice of w_j and our problem is to select a transition matrix P_{kj} so as to obey eq.(2.12). This can be achieved by imposing the condition of microscopic reversibility, that is

$$w_k P_{kj} = w_j P_{jk'}, \tag{2.14}$$

whatever j and k . In this case eq.(2.12) follows from

$$\sum_k w_k P_{kj} = \sum_k w_j P_{jk} = w_j \sum_k P_{jk} = w_j.$$

where the last equality is obtained with the aid of eq.(2.11). From eq. (2.14) we find now the constraint on the transition probabilities,

$$\frac{P_{jk}}{P_{kj}} = \exp \frac{-(U^{k} - U^{j})}{kT}, \qquad (2.15)$$

Eq. (2.15) still does not specify a unique Markov process. The prescription proposed by Metropolis et. al. [31] is to choose,

$$P_{jk} = a_{jk'}, \qquad \textit{if} \quad U^{(k)} \langle\, U^{(j)},$$

$$P_{jk} = a_{jk} \exp(-\frac{1}{kT}(U^{(k)} - U^{(j)}), \qquad \textit{if}\, U^{(k)} \rangle\, U^{(j)}.$$

and

$$P_{jj} = 1 - \sum_{k \neq j} P_{jk'} \qquad (2.16)$$

where a_{jk} are constants and $a_{jk} = a_{kj'}$

2.3.2 Realization of the Metropolis Monte-Carlo

In practice for simulation of liquid crystal properties this process can be realized in the following way. The state of the system is defined by the set of particle orientations, and the initial state is chosen in some suitable way. A particle is selected at random (see Appendix 2.1) or sequentially and a trial move is attempted in which the particle is rotated to a new orientation, usually distributed uniformly in a fixed ranged, say Δ, centred at the old orientation of the particle. The change in energy of the system due to this trial move is calculated. If the energy is increased (by an amount ΔU, say) the move is accepted with probability exp ($-\Delta U/kT$) and rejected with probability 1 - exp ($-\Delta U/kT$). This is achieved by comparing exp ($-\Delta U/kT$) with a random number uniformly distributed in (0,1). If the Boltzmann factor is greater than the random number the move is accepted, otherwise it is rejected. A sequence of configurations is generated and discarded until the initial energy of the system reaches an equilibrium value at which point a stage known as the production phase is entered. At this stage the process is repeated to form a sequence of states that are a **realization of Markov chain**.

The above procedure does not specify how rapidly the canonical distribution can be approached. It may be mentioned in this conection that the maximum displacement Δ must be chosen with some care. If too large, most moves will be forbidden, and if too small, the configuration will not change sufficiently. In either case it will then take longer to come to equilibrium. A suitable value of Δ is one that can give an acceptance - rejection ratio of unity.

In computer simulations the estimation of errors is of extreme importance. Clearly, properties can be recalculated at each new configuration generated by the Monte -Carlo chain thus providing very accurate averages. However, in general, the individual values forming the averages will be correlated with each other, thus any attemp to estimate the standard deviation will prove inaccurate. To overcome this problem, the simultaneous are normally broken up to steps (sometimes called 'macrosteps') over which time averages are calculated. The total averages of the property is then the averages of all the steps, and now assuming the sub averages to be uncorrelated, standard deviations can be evaluated. The length of each steps determines whether they are uncorrelated or not. Clearly they should be as long as possible, yet throughout the entire simulation there should be sufficient to provide a reasonable estimate of the standard deviation. Generally, the number calculated represents a compromise between these two factors.

2.3.3 Isothermal -Isobaric Monte Carlo Method

The simulation carry out in this thesis involved the application of the isothermal-isobaric ensemble . This NpT- method is applied to the system study of 500 particles interacting through Gay -Berne potential . This method will be consider in detail.

An advantage of the Monte Carlo method is that it can be readily adapted to the calculation of averages in any ensemble. Wood [37,38] first showed that the method could be extended to the isothermal-isobaric ensemble. In this ensembles the number of molecules, the temperature, and the pressure are held fixed while the volume of the simulation box is allowed to fluctuate. These original constant-NPT simulations were performed on hard spheres and disks, but McDonald [39,40] extended the technique to cover continuous potentials in his the study of Lennard-Jones mixtures. This ensemble was thought to be apopropriate for simulating mixtures since experimental measurements of excess properties are recorded at constant pressure and theories of mixing are often formulated with this assumption. The method has also been used in the simulation of single-component fluids [41] and also in the study of phase transitions [42]. In addition recently Luckhurst [43] had undertaken the NpT Monte-Carlo simulation in order to avoid the influenced of periodic images of the phase structure on Gay -Berne model mesogen, which initially was done on molecular dynamic simulation at constant volume.

The NpT Ensemble

In the constant-NPT ensemble in which an average quantity is defined by,

$$<M> = \frac{\int dV \int ds M \exp(-H/kT)}{Z}, \tag{2.17}$$

where Z is the configurational partition function; the integration is over the volume element dV and also over the volume element for the scaled coordinates ds. H is the energy function defined as,

$$H = U + pV - kTN \, lnV. \tag{2.18}$$

The criteria for acceptance or rejection in the Metropolis biased sampling method depends upon ΔH, the difference in the energy function between two consecutive ; This is,

$$\Delta H = \Delta U + p\Delta V - kTN \, lnV. \tag{2.19}$$

Since in the simulation, the box was kept orthogonal but the lengths of the three were allowed to vary independently hence changing the shape of the orthogonal box and its volume. In an isobaric move, uniform sampling of the log of the length was performed [44,45], choosing one side at a time. The function ΔH appropriate for this type of sampling scheme is,

$$\Delta H = \Delta U + p\Delta V - kT(N+1)\ lnV. \tag{2.20}$$

This allows the box to expand or contract efficiently. An isobaric move was performed once every 250 canonical moves each of these consisted of changing the position and the orientation of a particle simultaneously while keeping the box volume constant.

2.4 Thermodynamic Properties

The basic thermodynamic properties of a model system may be calculated as averages in any convenient ensemble.

The **isothermal compressibility,** β_T,

$$\beta_T = -V^{-1}(\partial V/\partial P)_P, \tag{2.21}$$

At constant T and P, both volume and energy fluctuations may occur. The volume fluctuations are related to the isothermal compressibility β_T,

$$<\delta V^2>_{NPT} = Vk_B\, T\beta_T, \tag{2.22}$$

The constant pressure **heat capacity** is defined as ,

$$C_P = (\frac{\partial H}{\partial T})_P, \tag{2.23}$$

In isothermal -isobaric ensemble the simplest specific heat at constant pressure C_P, formula may be obtained by calculating the ' instantaneous' entalpy (**H** + PV),

$$< \delta\ (\boldsymbol{H}+PV\ )2 >_{NpT} = k_B T^2 C_P,$$

$$C_p = \frac{<\delta(\boldsymbol{H}+PV)^2>_{NpT}}{k_B T^2}. \tag{2.24}$$

This equation can be split into the separate terms involving $<\delta \mathbf{H}^2>$, $<\delta V^2>$ and $<\delta \mathbf{H}\ \delta V>$.

The **thermal expansion coefficient** is defined as ,

$$\alpha_P = V^{-1}(\frac{\partial V}{\partial T})_P. \tag{2.25}$$

Finally, the thermal expansion coefficient α_P, may be calculated from the cross correlations of 'entalpy ' and volume .

$$<\delta V \delta(\boldsymbol{H}+PV\ ) >_{NpT} = k_B T^2 V \alpha_p. \tag{2.26}$$

Other quantities may be obtained by standard thermodynamic manipulations .

Orientational Order Parameters

The calculation of orientational order parameters is of particular importance in computer simulations of systems expected to exhibit liquid crystal phases. For a uniaxial mesophase where the orientation of the director is known, the second rank order parameter is simply,

$$\langle P_2 \rangle = (\frac{1}{N})\sum_{i=1}^{N} P_2(\cos\beta_i). \tag{2.27}$$

P_2 is the second Legendre polynomial where β_i is the angle between the orientation and the direction of a particle. The director could be fixed along a particular direction by, for example, the application of an external field. However in practice the director orientation is not known prior to the simulation. The usual route to the order parameter involves maximising the expression ,

$$\langle P_2 \rangle = (\frac{1}{N})\sum_{i=1}^{N} P_2(\boldsymbol{q}_i . \boldsymbol{n}), \tag{2.28}$$

with respect to the unit vector ***n***. Here $\mathbf{q}_i$ represents the unit vector of the i th molecule in the laboratory frame. This is acheived by rewritting as ,

$$\langle P_2 \rangle = (\frac{3}{2})\langle \boldsymbol{n} . \boldsymbol{Q} . \boldsymbol{n} \rangle, \tag{2.29}$$

where the tensor **Q** is

$$\boldsymbol{Q} = (\frac{1}{N})\sum_{i=1}^{N} \boldsymbol{q}_i \boldsymbol{q}_i - (\frac{1}{3})\boldsymbol{I}. \tag{2.30}$$

I is the moment of inertia tensor which derives from the equations of classical rotational dynamics [46] and so, for example,

$$\boldsymbol{Q}_{xz} = (\frac{1}{N})\sum_{i} \boldsymbol{q}_{ix} \boldsymbol{q}_{iz}, \tag{2.31}$$

where **Q** tensor with respect to the laboratory axis. In order to locate the director it is important to diagonalised the **Q**- tensor into the director frame. In the situation that **n** is parallel to the z axis, **Q** is then symmectric and traceless and for cylindrical phase the tensor takes the form of

$$\begin{matrix} -(\frac{1}{3})\langle P_2\rangle & 0 & 0 \\ 0 & -(\frac{1}{3})\langle P_2\rangle & 0 \\ 0 & 0 & (\frac{2}{3})\langle P_2\rangle \end{matrix} \tag{2.32}$$

It is clear then that the orientation of the director in the space fixed axes is the eigenvector corresponding to the largest eigenvalue, $\lambda_{\max}$ obtained from the diagonalisation of **Q**. The second rank order parameter is obtained from the largest eigenvalue as,

$$\langle P_2 \rangle = (\frac{3}{2})\lambda_{Max}. \qquad (2.33)$$

Ideally, the**Q** tensor should be constructed and diagonalised at each time step and $<P_2>$ calculated from the value of $\lambda_{\max}$ averaged over the whole simulation. But this is of course a time consuming. Therefore the Q is collected and averaged over a macro-step. The macrostep size must be appreciably small enough to avoid significant director fluctuation [47]. A problem with the above procedure is that it necessarily predicts a non -zero order parameter for the isotropic phase due to finite size system. Eppenga and renkel [48] have shown that the use of $\lambda_{\max}$ leads to an isotropic order parameter of order $1 / \sqrt{N}$ while that obtained from the middle order parameter has associated errors of order 1/N. However, $\lambda_{\max}$ is a more accurate indication of the order in the nematic phase and is the one normally preferred.

2.5 Structural Properties

The Radial Distribution Function

The structure of simple monoatomic fluids is characterized by a set of distribution functions for the atomic positions , the simplest of which is the pair distribution function $g_2(r_1, r_2)$, or $g_2(r_{ij})$ or simply $g(r)$. It is defined by intergrating the configurational distribution function over all but two of the atomic coordinates [49],

$$g_2(r_1,r_2)=N(N-1)/\rho^2 Z_N \int [\exp - U(r_1,r_2,...r_N)/kT]dr_3..dr_N, \qquad (2.34)$$

where ρ is the number density. This function gives the probability of finding a pair of atoms at a distance r apart, relative to the probability expected in an ideal gas. It is worth considering a few limiting situations. At large separations, the position of atoms are uncorrelated and so g (r) tends to the the ideal gas value of one. For atoms with a hard impenetrable core there is a vanishing probability of finding a second atom nearer than a minimum distance σ from the first one, that is

$$g(r) = 0, \qquad r < \sigma \qquad (2.35)$$

A plot of g (r) will roughly take the form shown in Figure 2.4. An example of a typical pair distribution function for the Lennard- Jones liquid close to it triple point shown in Figure 2.5[24]. The sucessive peaks provide an indication of the short range order and can be used to identify average shells of neighbours. These peak gradually decay as the atomic positions become uncorrelated. For a solid the peaks continue to oscillate even at large separations. In an idealized solid they would be delta functions but thermal oscillations will obviously tend to smear them out.

In the simulation, the pair distribution function is calculated by constructing a histogram of all the minimum image particle separations where each bin has a width of δr and extends from r - δr/2 to r + δr/2. To obtain g(r) each bin is divided by the average number of atoms in the same interval in an ideal gas at the same density. This is calculated from,

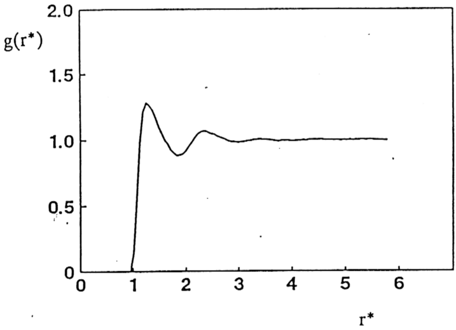

Figure 2.4 A typical Radial distribution function for a liquid.

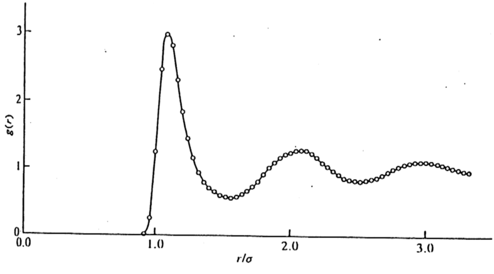

Figure 2.5 Pair distribution function for the Lennard - Jones fluid close to the trip point.

$$
\begin{aligned}
n_{id} &= (4\pi\rho/3)[(r+\delta r/2)^3-(r-\delta r/2)^3] \\
&= (4\pi\rho/3)[3r^2\delta r+\delta r^3/4], \qquad (2.36)
\end{aligned}
$$

Since δr is small the term involving δr^3 is often neglected.