

FLUIDS WITH ANGLE-DEPENDENT  
POTENTIALS

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## PREFACE

This dissertation is an account of work carried out between February 1980 and February 1983 at the Department of Applied Mathematics, Research School of Physical Sciences, Australian National University, for the degree of Doctor of Philosophy.

All the work in Chapters 2 to 7 is a result of close collaboration between my supervisor, Dr Derek Chan and myself. In section 2.3 and Chapter 4, the work is a joint effort with Steven Carnie and Derek Chan; while that in section 5.3 is in collaboration with Dr Derek Chan and Dr John Mitchell.

This work has not been submitted to any institute of learning for any degree.



Glen Walker

## PUBLICATIONS

1. 'Thermodynamic properties of a fluid of hard spheres with water-like dipole and quadrupole moment', Chem. Phys. Lett., 79, 588, 1981. (with Steve Carnie and Derek Chan)
2. 'Statistical Mechanics of Ion-Dipole-Tetrahedral Quadrupole Mixtures', Molec. Phys., 43, 1115, 1981. (with Steve Carnie and Derek Chan)
3. 'A non-linear truncation scheme for the Ornstein-Zernike equation for dipolar fluids', Molec. Phys., 47, 881, 1982. (with Derek Chan)

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## ABSTRACT

In this thesis integral equation techniques, developed in liquid state physics over the last twenty years, are applied to a study of fluids with angle dependent potentials.

In particular, multipolar fluids and liquid crystals are studied. There are many similarities and contrasts in the mathematical formalism and physical principles used in modelling these two fluids. These are introduced in Chapters 1 and 2.

In Chapter 3, an isotropic system of dipolar hard spheres is studied using a non-linear truncation of the hypernetted chain closure of the Ornstein-Zernike equation. This enables dipolar fluids with low density to be investigated. The mathematics developed to do this also enables the Percus-Yevick closure to be used. The effect of water-like quadrupole moments on dipolar hard spheres is discussed in Chapter 4. It is shown that schemes developed for axial quadrupoles are easily adapted to water-like quadrupoles. The results indicate that the quadrupole moment is an important influence on the macroscopic properties of water.

Many of the important applications of polar fluids are a result of their behaviour in external fluids. A number of interesting issues arise when one tries to develop a formalism for describing the effects of a field on polar fluids. Some of these are discussed in Chapter 5.

In the final two chapters, the properties of liquid crystals are determined using an expression for the free energy in which the

molecular properties are included via the direct correlation function. In a certain limit this expression is the same as that of the successful Maier-Saupe theory. Using this, one can describe the isotropic-nematic transition, elastic behaviour and the alignment at surfaces in terms of the direct correlation function and hence the molecular properties.

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## CHAPTER 1

### 1.1 Introduction

It is difficult to relate the properties of liquids to the properties of the individual molecules. The high density and the lack of a long-range structure in liquids prevent the techniques which have been used with reasonable success for either gases or solids from being used for liquids.

In this thesis, attention is focussed on those liquids in which the intermolecular interaction depends on the orientations of the molecules. In particular, polar fluids (i.e. fluids with permanent electrical moments) and liquid crystals are considered. Because of the complexities mentioned in the preceding paragraph, the model system of the liquid needs to be very simple.

The physical principles of the behaviour of polar liquids and liquid crystals are described in this chapter with the mathematical formalism being developed in later chapters. The mathematics needed to describe the anisotropic interactions in these liquids (Chapter 2) can become quite complex and a reasonable understanding of the physics of the system is needed to understand the approximations used. Even though some of the symmetry properties of molecular interaction can help to simplify the mathematics, the problem of describing these liquids is still a daunting task.

Chapters 3 to 5 embody the main work on polar liquids while in Chapters 6 and 7 liquid crystals are studied. In these chapters the approximations are outlined and the calculations performed.

## 1.2 Modelling Liquids

In most liquids — liquid hydrogen and helium being the major exceptions — the relationship between the microscopic properties of the constituent molecules and the macroscopic properties of the liquid can be described with classical statistical mechanics. The Hamiltonian used is one in which the effects of intra-molecular motion has been averaged. (For the liquid crystal work, bending of the alkyl chains may need to be included but at this stage shall be ignored.) The Hamiltonian for  $N$  molecules can then be written as

$$H_N = \sum_{i=1}^N \frac{p_i^2}{2m_i} + u(1,2,\dots,N) \quad (1.1)$$

where  $u(1,2,\dots,N)$  is the interaction potential of  $N$  molecules situated at  $\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N$  and having orientations  $\omega_1, \omega_2, \dots, \omega_N$  and  $p_i$  and  $m_i$  are the absolute value of the momentum and mass of the  $i$ th particle. Here  $i$  denotes the position  $\underline{r}_i$  and the orientation  $\omega_i$ .

The properties of the individual molecules are represented by the term  $u(1,2,\dots,N)$ . Our approach is to use an expression for  $u(1,2,\dots,N)$  which involves the properties of the molecule and then use statistical mechanics with the Hamiltonian (1.1) to calculate the liquid properties.

For a pair of argon atoms,  $u(1,2)$  can be approximated by

$$u(1,2) = u_0(|\underline{r}_1 - \underline{r}_2|) \quad (1.2)$$

where  $u_0(r)$  is depicted in Fig. 1.1.



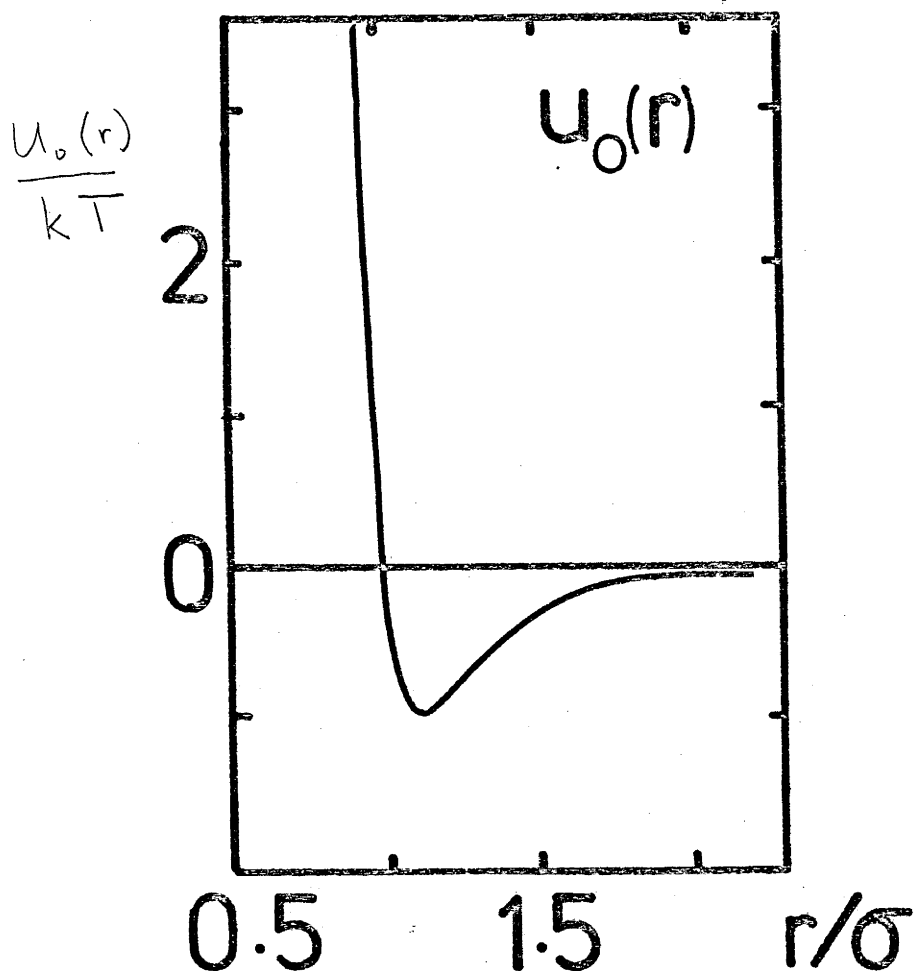


Fig. 1.1 Interaction potential  $u_0(r)$  between two argon atoms separated by  $r$ .

Here  $\sigma$  has roughly the same value as the diameter of the argon atom. There is a short-range repulsion which prevents the separation of the nuclei of the argon atoms from ever becoming much less than the molecular diameter. The effect would be similar to bringing two soft spheres together. Since the repulsive component of interaction between two argon atoms is similar to the interaction of two soft

spheres, the argon atom will be described in this thesis in terms of a soft sphere. Superimposed on the repulsion is a longer-ranged van der Waals attraction.

Liquid argon is a particularly simple example of a fluid since the interaction between the constituent atoms depends only on the separation of the atoms.

### 1.3 Angle-dependent Potential

For the carbon dioxide molecule, the analogy with the sphere is less appropriate than an ellipsoid or the spherocylinder. To illustrate the problem of such a shape dependence, a fluid of hard spherocylinders is considered. Two spherocylinders are depicted in Fig. 1.2.

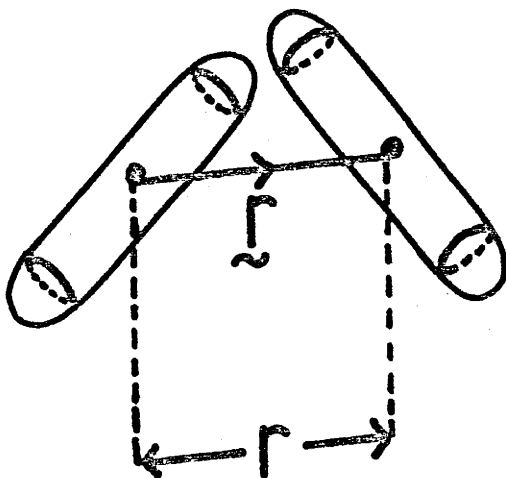


Fig. 1.2 Two hard spherocylinders separated by  $r$ .

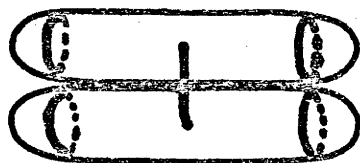
Whether or not two such particles touch depends not only on the

separation  $r$  between the centres of the two particles but also on the following orientations:

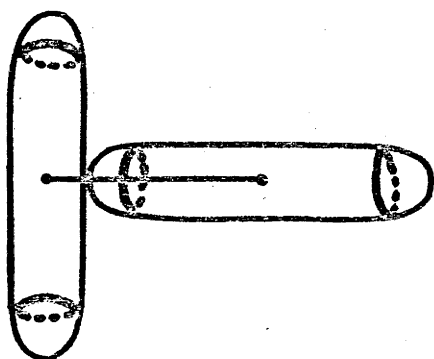
- (i) the orientation  $\omega_1$  of molecule 1
- (ii) the orientation  $\omega_2$  of molecule 2
- (iii) the orientation  $\underline{r}$  of the intermolecular axis.



(a)



(b)



(c)

Fig. 1.3 Arrangements of spherocylinders which are in contact even though the separations are different.

This can be seen by noting that the particles arranged as illustrated in Fig. 1.3(a-c) are in contact even though their inter-particle separations are different. Such a point may seem trivial until one needs to describe the macroscopic properties of a dense system of these particles. Any statistical mechanical treatment must omit configurations in which two such bodies overlap and this demands the knowledge of not only the positions of the particles but also their orientations. Statistical mechanical techniques that have been developed for 'simple' fluids must be adapted to deal with orientations, yet still remain computationally efficient. This is a difficult problem.

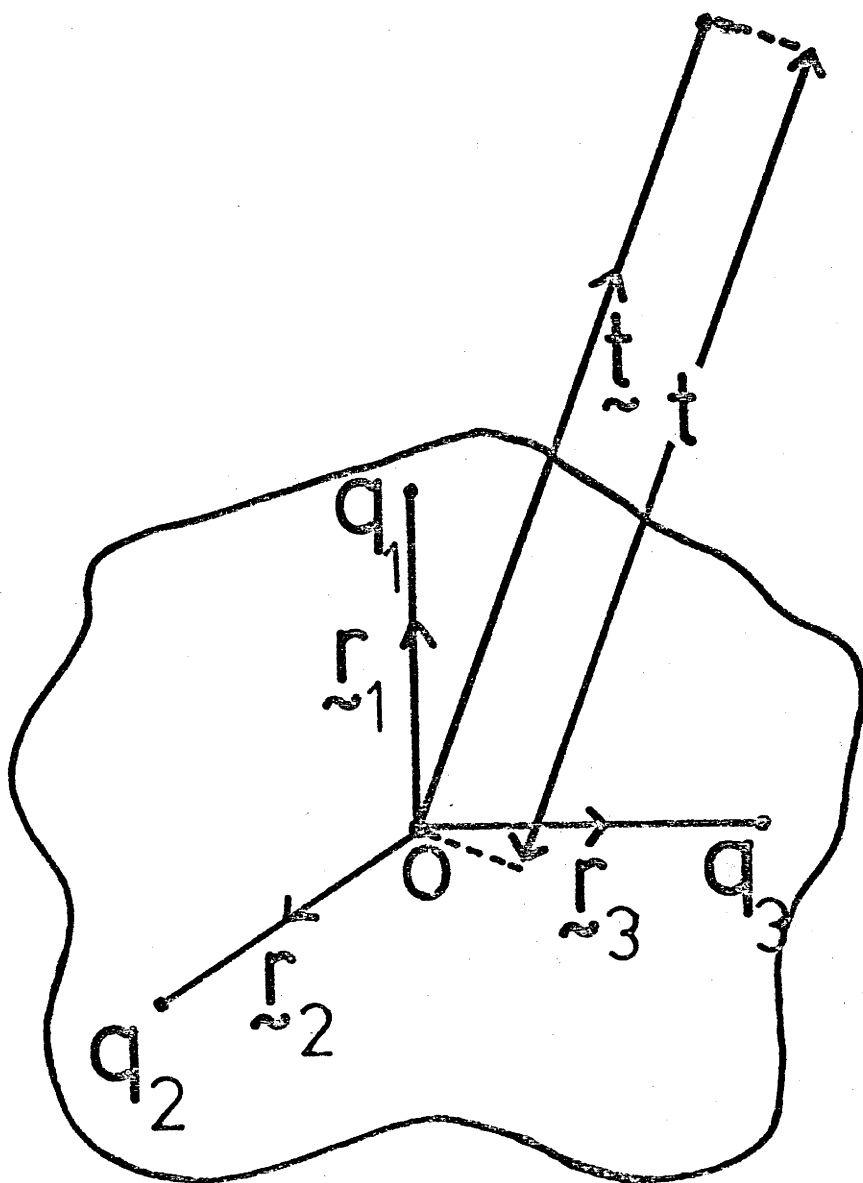
Similar problems occur for any fluid in which the interactions depend on the orientations (i)-(iii). For example, fluids in which the molecules have permanent multipoles would experience similar problems. In the next section the interactions of such molecules are discussed.

#### 1.4 Electrostatic interactions

The interaction between a pair of argon atoms (<sup>an</sup> ~~argon~~ atoms) has no permanent multipole) consists of a short-ranged repulsion and a longer-ranged van der Waals attraction. In most molecules, however, there are permanent electrical moments which can interact with the electrical moments of other molecules. Such a moment is the result of an asymmetry of the electron distribution. In our idealised model, we view the electrical moment as being imbedded in the body representing the molecule. This added interaction is then given by the laws of electrostatics.

The electrostatic potential at  $\underline{r}$  due to charges imbedded in a body (as illustrated in Fig. 1.4) will ~~asymptote~~ <sup>behave</sup> for large  $r$  as

Fig. 1.4 Charges  $q_1, q_2, q_3$  situated at  $\vec{r}_1, \vec{r}_2, \vec{r}_3$ .



$$\psi(\underline{t}) = \frac{Q}{t} + \frac{\underline{\mu} \cdot \underline{t}}{t^3} + \sum_{i,j} \theta_{ij} \frac{t_i t_j}{t^5} + \dots \quad (1.3)$$

This expression uses Cartesian co-ordinates. The terms  $Q$ ,  $\underline{\mu}$ ,  $\underline{\theta}$  are respectively given by

$$Q = \sum_{i=1}^N q_i \quad (1.4)$$

$$\underline{\mu} = \sum_{i=1}^N q_i \underline{r}_i \quad (1.5)$$

$$\theta_{ij} = \frac{1}{2} \sum_i q_i (3x_i x_j - r^2 \delta_{ij}) \quad (1.6)$$

The  $N$  charges  $q_i$  are situated at  $\underline{r}_i = (x_1, x_2, x_3)^T$ . Also

$$r = |\underline{r}| \quad (1.7)$$

$$t = |\underline{t}| \quad (1.8)$$

$Q$  is the total charge,  $\underline{\mu}$  is the permanent dipole, and  $\underline{\theta}$  is the quadrupole<sub>moment</sub>. These electrical moments will be used frequently during this thesis.

The electrostatic field can then be written as the sum of the fields due to the various electrical moments. For example the electric field  $\underline{E} (= -\underline{\nabla} \psi)$  due to a dipole is shown in Fig. 1.5. Here the arrow represents the direction of  $\underline{\mu}$

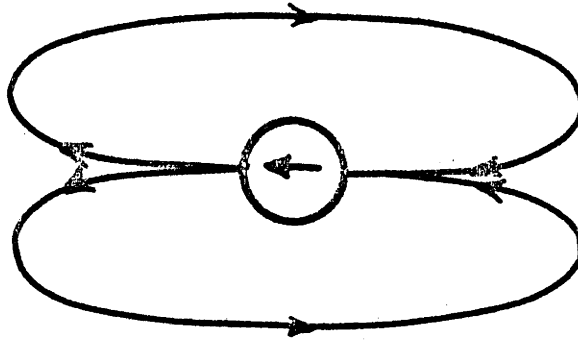


Fig. 1.5 Field due to Dipole

For the special case of all the charges lying on a single line the quadrupole is given by

$$\Theta_L = \begin{pmatrix} \frac{1}{2} \Theta_L & 0 & 0 \\ 0 & \frac{1}{2} \Theta_L & 0 \\ 0 & 0 & -\Theta_L \end{pmatrix} \quad (1.9)$$

$$\Theta_L = - \sum_{i=1}^N q_i z_i^2 \quad (1.10)$$

Here the z-axis is parallel to the line of charges and hence to the dipole moment. The field due to such a quadrupole moment is illustrated in Fig. 1.6 .

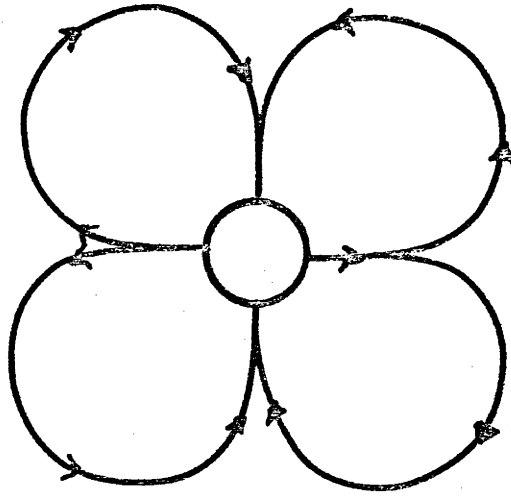


Fig. 1.6 Field due to Linear Quadrupole

To understand the interactions between charge distributions, one not only needs to know the fields produced by the charges but also their reaction to an applied electric field. For instance certain orientations of the charge distribution are energetically less favourable than others. To calculate favourable orientations, one needs to know the electrostatic energy:

$$E = Q \psi(0) + \underline{\mu} \cdot \underline{\nabla} \psi(0) + \frac{1}{3} \sum_i \sum_j \theta_{ij} \frac{\partial^2 \psi(0)}{\partial x_i \partial x_j} + \dots \quad (1.11)$$

Here cartesian co-ordinates have been used.  $\psi(0)$  is the electrostatic potential at the centre of the charge distribution.



The first term is the energy of a charge  $Q$  in an electrostatic potential  $\psi(o)$ . The second term is the familiar  $-\mu|\underline{E}|\cos\theta$  for the interaction of a dipole with the electric field  $\underline{E} = -\underline{\nabla}\psi(o)$  where  $\theta$  is the angle between the dipole and the electric field. The third term is the interaction of the quadrupole with the gradient of the electric field.

One can see that it is energetically favourable for the dipole to lie parallel to the electric field and for a linear quadrupole to lie parallel to the direction in which the field is changing most rapidly (i.e. perpendicular to the field lines).

By knowing that a dipole produces a field as illustrated in Fig. 1.5 and that it is energetically favourable for another dipole in the vicinity of the first dipole to lie parallel to the local field, one can see that the arrangements of dipoles illustrated in Fig. 1.7 will themselves be energetically favourable. Each of the dipoles lies in the other's field. This sort of analysis will be useful when discussing arrangements of molecules in liquids.

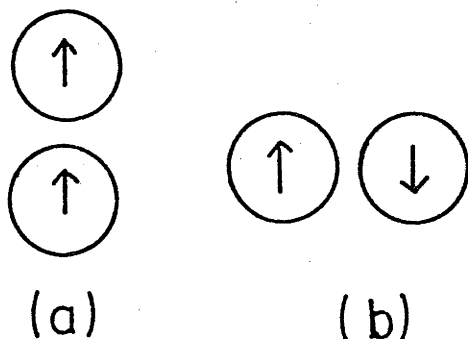


Fig. 1.7 Energetically favourable arrangements of dipoles.

Finally, since the field produced by a charge distribution and the reaction of a charge distribution to an applied field can be written entirely in terms of the electrical moments, we shall therefore characterize a given charge distribution as the sum of electrical moments

i.e. total charge + dipole moment + quadrupole moment + ... .

Higher multipoles are only important in the intermolecular interactions if the molecules are separated by very small distances. For a fluid it is expected that the effect of the multipoles higher than quadrupole on the macroscopic properties is negligible.

### 1.5 Correlation functions

In section 1-2 to 1-4 the relation between molecular properties and molecular interactions have been described. The next stage is to consider the effects of molecular interactions on macroscopic properties of liquids. To do this, we make use of the pair correlation function  $g(1,2)$  defined by

$\rho(1) g(1,2) \rho(2) d\mathbf{r}_2 \equiv$  probability that a molecule can be found in the volume  $d\mathbf{r}_1$ , about  $\mathbf{r}_1$ , and within an orientation  $d\omega_1$  of  $\omega_1$ , and similarly a molecule can be found in a volume  $d\mathbf{r}_2$  about  $\mathbf{r}_2$  and within an orientation  $d\omega_2$ . The notation 1 will denote the coordinate  $(\mathbf{r}_1, \omega_1)$  and  $d\mathbf{l}$  the infinitesimal  $d\mathbf{r}_1 d\omega_1$ . Here  $\rho(1)$  is the number of particles per unit volume with position  $\mathbf{r}_1$  and orientation  $\omega_1$ .

Some of the qualitative features of  $g(1,2)$  are immediately obvious. Consider the arrangement of particles in Fig. 1.8. If the

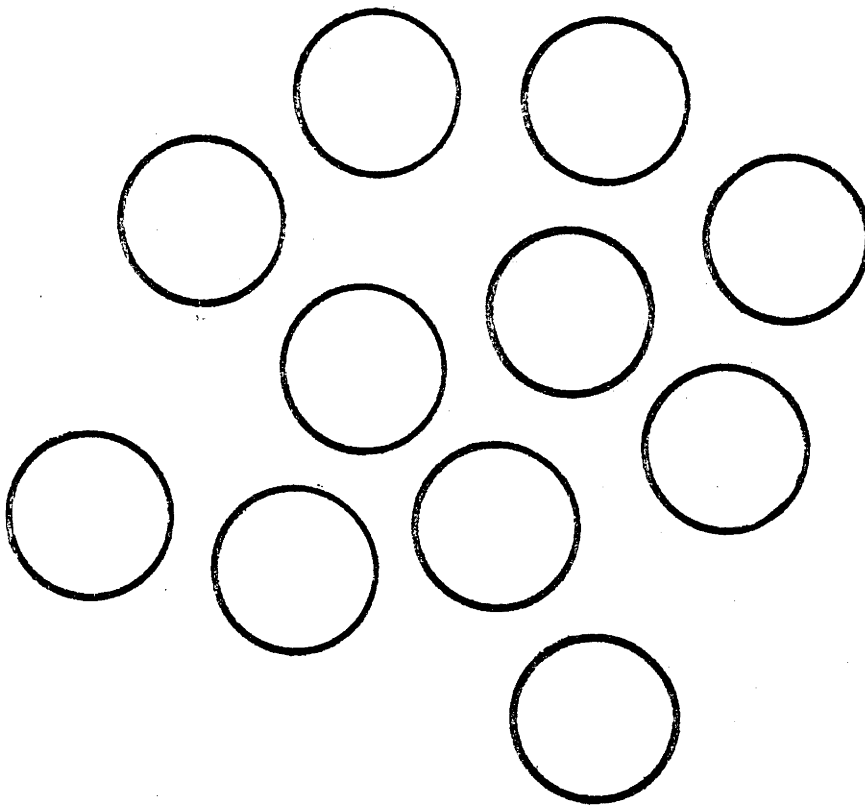


Fig. 1.8 Possible arrangements of molecules in a Liquid

spheres are hard, there is no possibility of the centres of the spheres being closer than the sphere's diameter  $R$ . Thus, for separations less than  $R$

$$g(1,2) = 0 \quad .$$

The internal pressure of this system results from the tight packing arrangement. This means that there is a strong possibility of finding pairs of spheres separated by distances in the range  $R$  to  $R'$ , whereas relatively few pairs of spheres are separated by distances in the range  $R'$  to  $R''$ . The correlation function for such a fluid is drawn in Fig. 1.9.

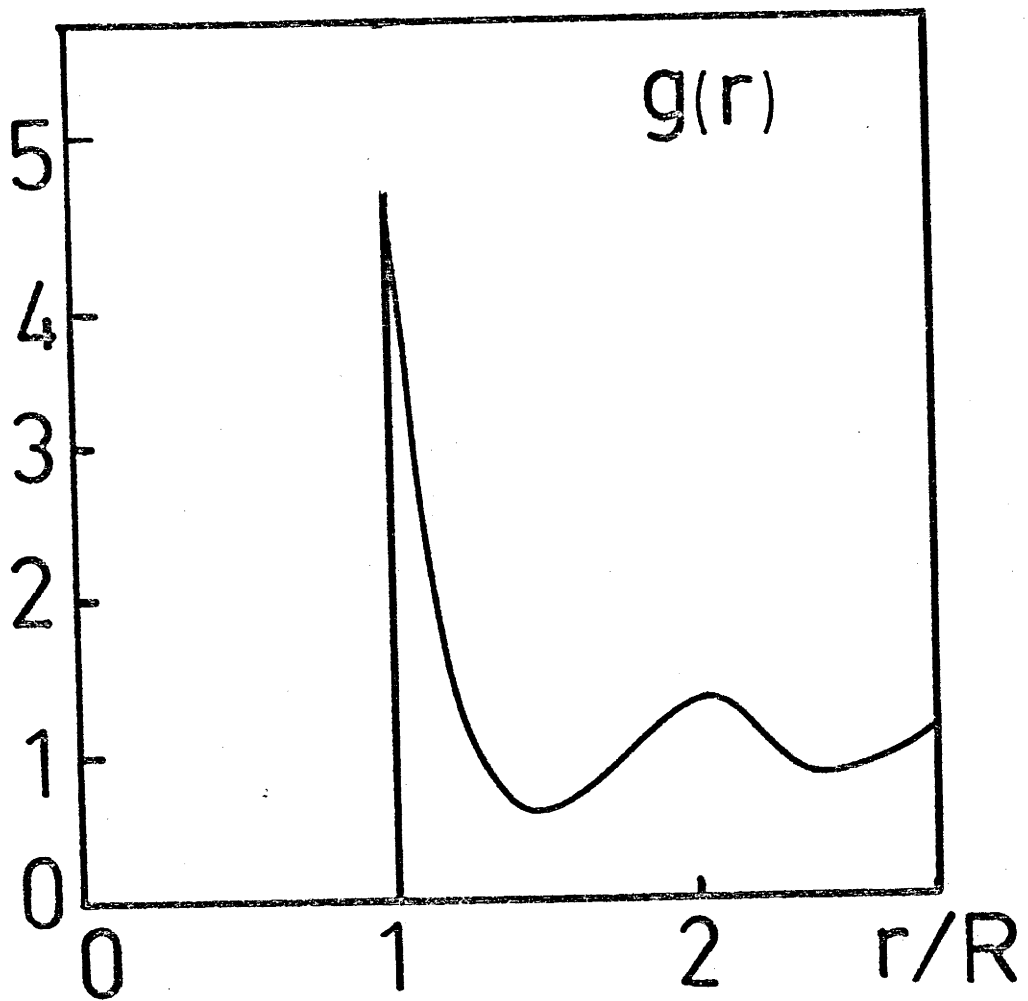


Fig. 1.9 Hard sphere correlation function

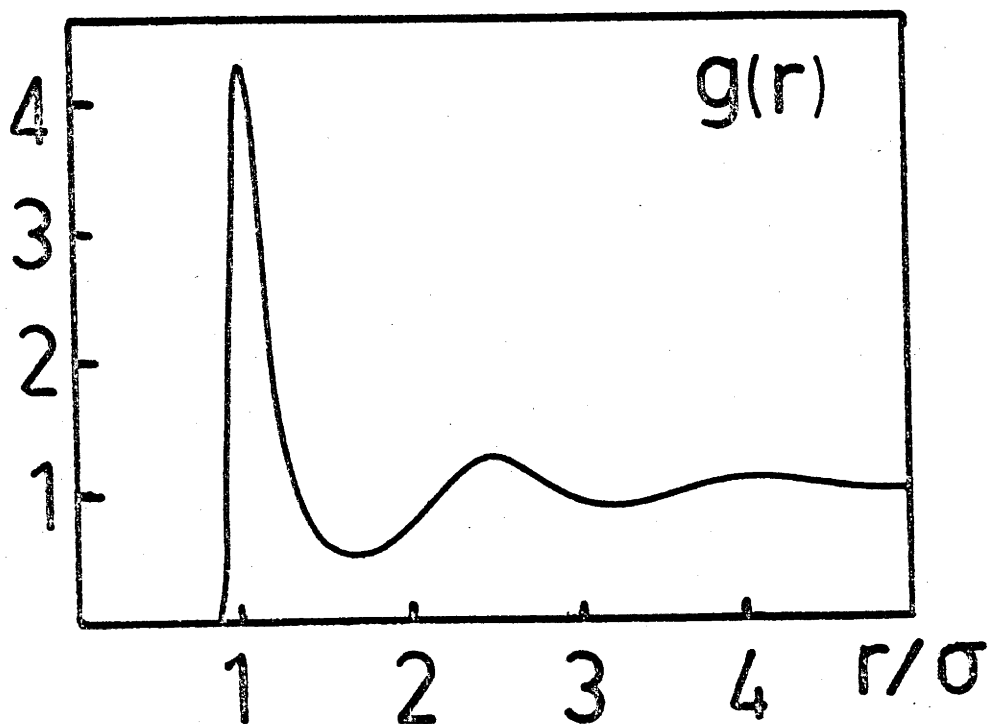


Fig. 1.10 Soft Sphere correlation function

If the spheres are soft, they can be separated by distances less than  $R$ . The correlation function for soft spheres should resemble that drawn in Fig. 1.10. This is very similar to the correlation function of liquid argon. At the high densities found in liquids, it seems that the correlation function is mainly determined by the short-ranged repulsive core rather than the slowly varying components of the potential such as the van der Waals attraction. This notion, originally used by van der Waals is the basis of many numerical schemes in liquid state physics.

If the spheres are imbedded with dipoles, then the correlation function has an added complication. The orientation of the dipole imbedded in one particle can influence the orientation of the surrounding dipoles. The correlation function must reflect this orientation dependence. It must depend on the orientation of each particle as well as the orientation of the intermolecular axis. Averaging over these orientations yields a function similar to those shown in Figures 1.9 and 1.10 depending whether the spheres are hard or soft. Again, this agrees with van der Waals notion of the liquid i.e. the number of particles at a distance  $r$  from any given particle is largely determined by the short-ranged repulsive force rather than the longer-ranged dipole-dipole interaction. This principle will be used frequently in this thesis.

Macroscopic properties such as dielectric constant, pressure, internal energy and free energy can be written in terms of the correlation function. The strategy of liquid state physics is to calculate the interaction energy from the molecular properties and to use this to calculate the correlation function which in turn yields pressure, internal energy etc.

## 1.6 Dipolar fluids

Consider a fluid in which the molecules have a permanent dipole moment. A simple model of the molecule is a hard or soft sphere imbedded with a dipole. As will be seen in later chapters the effect of the higher multipolar interaction in liquids can be appreciable. There are, however, a number of reasons for neglecting higher moments at this stage. It is of interest to investigate the effects of the dipole-dipole interaction without the complicating effects of dipole-quadrupole interactions, quadrupole-quadrupole interactions, etc. Secondly the long-range nature of the dipole-dipole interaction can cause problems with numerical schemes, so it is important to develop a scheme that can handle the interaction. If this can be done, one can have confidence in applying these schemes to more complicated models.

Recently, a large amount of work has been devoted to the statistical mechanical study of dipolar fluids. This work has mainly centred on the calculation of the pair correlation functions and dielectric properties. While a certain degree of success has been achieved in modelling most aspects of the correlation functions, the same cannot be said for those aspects concerned with dielectric behaviour.

The problem is twofold. The dipole-dipole interaction is both long-ranged and angle-dependent. The long-ranged nature of the potential implies that schemes such as computer simulations that truncate the spheres of influence have difficulty modelling the dipolar system. The angle dependence is partly offset by the van der Waals concept of liquids. The fact that the structure is

mainly determined by the repulsive forces rather than the dipole-dipole interaction can be used as a basis for perturbation-like schemes.

However as the density is decreased, the gaps between the particles become larger and the longer-ranged component of the potential becomes relatively more important. For a purely dipolar fluid, the correlation function will approach

$$g \sim \exp(-\beta U_{DD}) \quad (1.12)$$

where

$$\beta = 1/kT \quad (1.13)$$

and  $U_{DD}$  is the dipole-dipole interaction potential. In Chapter 3 a numerical scheme will be developed that has this correct low density limit and yet should be reasonably accurate for higher densities. The scheme can also be used for investigating the shortcomings of using a perturbation-like scheme based on van der Waals concept of liquids. It can then hopefully be used in a robust scheme that gives reasonable results over a wide range of densities and dipole moments.

### 1.7 Dipoles in a Field

It is well known that an external field will increase the alignment of a system of dipoles. For an ideal dipolar gas of density  $\rho_0$ , the average number of dipoles whose dipolar axis makes

an angle  $\theta$  with the external field  $\tilde{E}$  will be

$$\rho(\theta) = \rho_0 \exp(-\beta |\tilde{E}| \cos\theta) \quad (1.14)$$

$$\beta = 1/kT$$

At higher densities there will be a distortion of this due to the interaction between dipoles. For small fields,  $\rho(1)$  will be given by

$$\rho(1) = \rho_0 \exp(-\beta |\tilde{E}| \cos\theta + \int d2 \, c(1,2) \rho(2)) \quad (1.15)$$

where  $c(1,2)$  is the direct correlation function of the bulk system. [ $c(1,2)$  will be discussed in chapter 2.] Thus the density  $\rho(1)$  depends on correlations in the liquid and similarly the correlations depend on the density  $\rho(1)$ . Much of the previous work has been concerned with the density rather than the correlation. In Chapter 5, the latter is studied.

To gain some understanding of correlations in an external field consider the effect of an external field on the field lines produced by a single dipole. The effect of the external field is to distort the local field lines in such a way to decrease the likelihood of a dipole opposing the field. As the field becomes stronger the dipole is much more likely to lie parallel to the external field. One can see that the other dipoles are likely to lie end to end to any given dipole and almost none will lie anti-parallel to the field or lie side by side to a given dipole. For example, dipoles A and B in Fig. 1.11 will attract each other while A and C will repel each



other. Because it lies anti-parallel to the external field, dipole D will be energetically unfavourable. The net effect is the production of chains that repel each other. This chain formation has been observed in the so-called 'ferro-fluids' - colloidal dispersions of ferromagnetic grains.

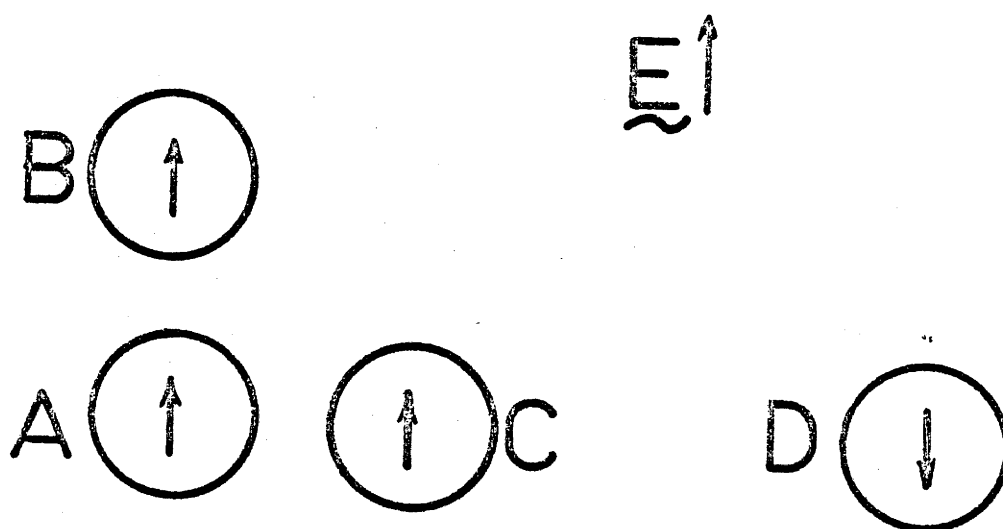


Fig. 1.11 Dipoles A,B,C,D in an external field

### 1.8 Tetrahedral Quadrupole

As the density increases the separations between particles become smaller, and the relative importance of the quadrupole compared to the dipole increases. At liquid densities it may be

expected that the effect of quadrupolar interactions are significant.

Previous calculations have only investigated the linear (axial) quadrupole i.e. the quadrupole of a series of charges lying on a single line. The field due to such a quadrupole is shown in Fig. 1.6. In an applied field, such a quadrupole favours a direction perpendicular to the field whereas the dipole favours a direction parallel to it. If the permanent charge distribution of a particle is such that it has a dipole moment and a linear quadrupole moment, then it favours a direction at an angle to the field, the angle depending on the relative strengths of the dipole and quadrupole. Since the quadrupole decreases the alignment of the dipoles with the field, it can be expected that its neglect can lead to an overestimate of the dielectric constant. Numerical schemes [1] have shown that this overestimate can be appreciable even for moderate values of quadrupole moment.

If in our simple picture of the molecule, the charges do not lie on a single line, then the quadrupole is more complicated. This would be the case with most molecules. For example, consider the charge distribution in Fig. 1.12. Here, the charges all lie on the vertices of a regular tetrahedron. The negative charges are lying in the y-z plane (plane of the page) and the positive charges are lying equidistant from the y-z plane in the x-z plane. The field due to the quadrupole moment of such a particle is illustrated in Fig. 1.13. Such a quadrupole shall be termed a 'tetrahedral' quadrupole.

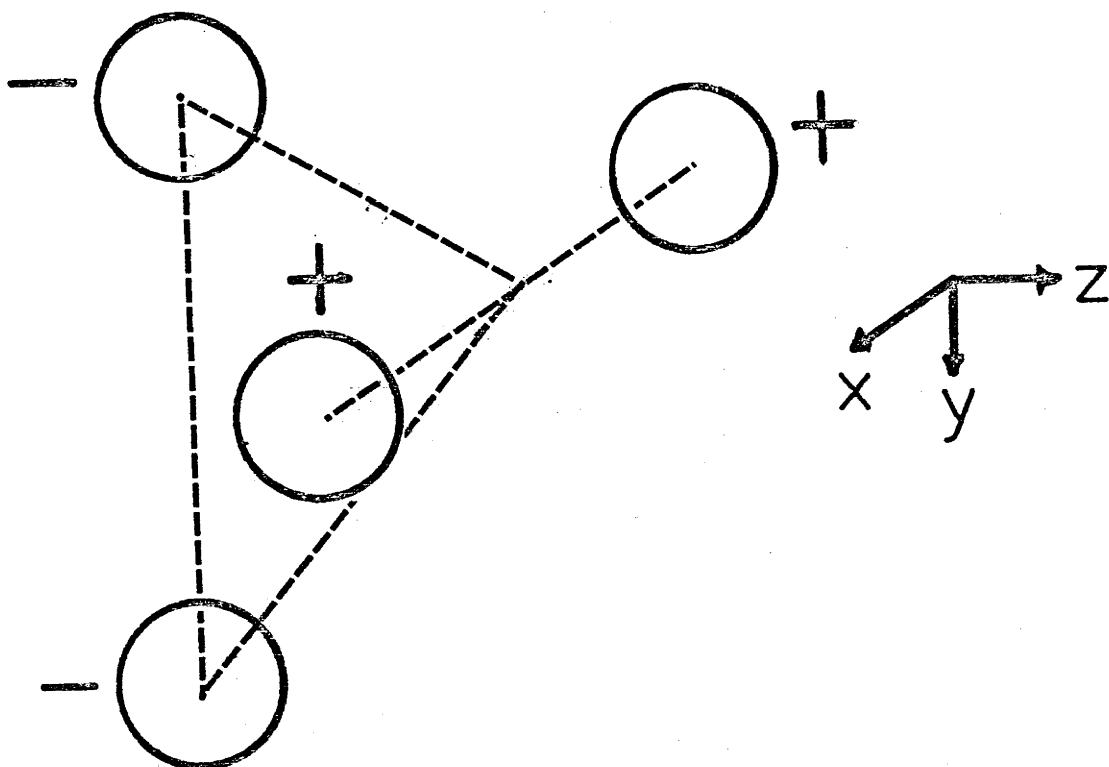


Fig. 1.12 Arrangement of charges resulting in a tetrahedral quadrupole

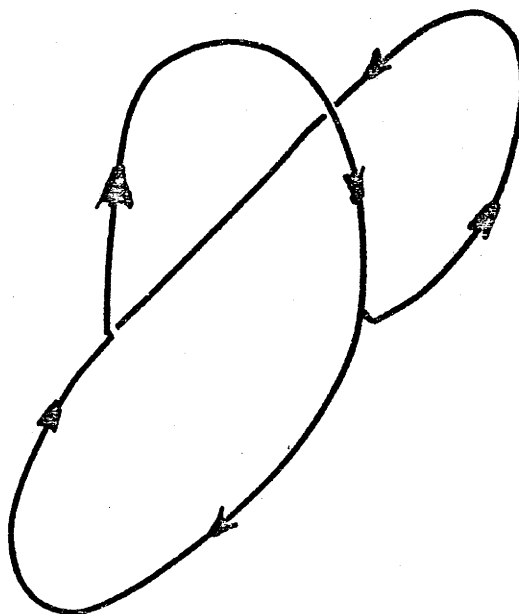


Fig. 1.13 Field due to Tetrahedral Quadrupole

Unlike the linear quadrupole it is not cylindrically symmetric, and so an extra angle is needed to the field due to such a quadrupole moment.

The effect of an external electric field on such a particle is also more difficult to describe. Perhaps the simplest expression for the electrostatic energy in a field  $\underline{E}$  is given in terms of the molecular frame (see Fig. 1.12)

$$E = -\frac{1}{3} \left( \frac{\partial E}{\partial x} x - \frac{\partial E}{\partial y} y \right) \Theta \quad (1.15)$$

The particle will tend not to align with the field but its orientation will depend on the overall symmetry of the local field rather than the gradient in just the one direction, as is the case with the linear quadrupole.

In Chapter 4 we find that in spite of the decrease in symmetry, the techniques that have been used for linear quadrupoles can just as easily be used for 'tetrahedral' quadrupoles and dipoles.

This is an important step, since the quadrupole moment of water resembles that of the tetrahedral quadrupole. We can gain some ideas about the importance of the dipole and quadrupole moments of the water molecule in determining the properties of water. For example, we would like to know what extent the quadrupole moment determines the near tetrahedral packing of the water molecules. The quadrupole could also be important in determining the dielectric behaviour of water.

### 1.9 Liquid Crystals

Thermotropic liquid crystals do not have an isotropic liquid-solid transition as the temperature falls but exhibit a number of transitions from an isotropic liquid phase through ordered phases to a solid phase. In the ordered phases, there is no lattice structure as in the solid, but there is considerable rotational order. For example, in the 'nematic' phase the molecules tend to align with a certain direction  $\hat{n}$  called the 'director'. Yet, the positions of the centres of the molecules are disordered as in a liquid. (See Fig. 1.14)

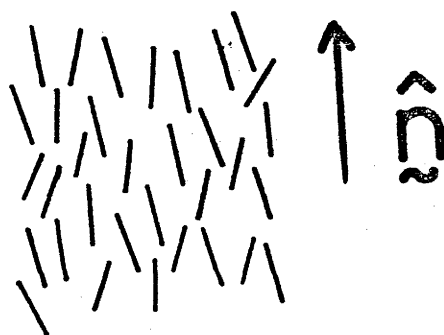


Fig. 1.14 Arrangement of molecules in a nematic. The director in  $\hat{n}$

The isotropic-nematic transition has a number of interesting features. It is a first order phase transition yet in many ways resembles a second order transition. There are discontinuities in the density, the internal energy and entropy, but these are small. The change in entropy, for example is only about 0.8 cal/mol °K as

compared to 25 cal/mol °K in solid-liquid transitions in similar organic materials.

Liquid crystal display 'pre-transitional' behaviour, in that the response functions of the isotropic phase (e.g. induced birefringence) begin to diverge as the critical temperature,  $T_c$ , is approached from above. The phase change occurs before the divergence is observed. This pre-transitional behaviour is usually not found in first-order phase transitions.

It is thought that the small change of entropy means that fluctuations are much more likely and this leads to pre-transitional behaviour. The arrangement of the molecules in the isotropic phase just above  $T_c$  does not resemble that in Fig. 1.15 as much as that in Fig. 1.14 ~~1/2~~.

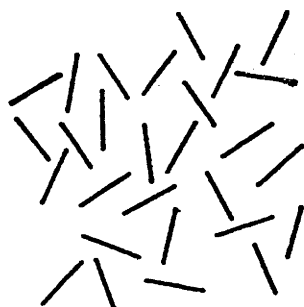


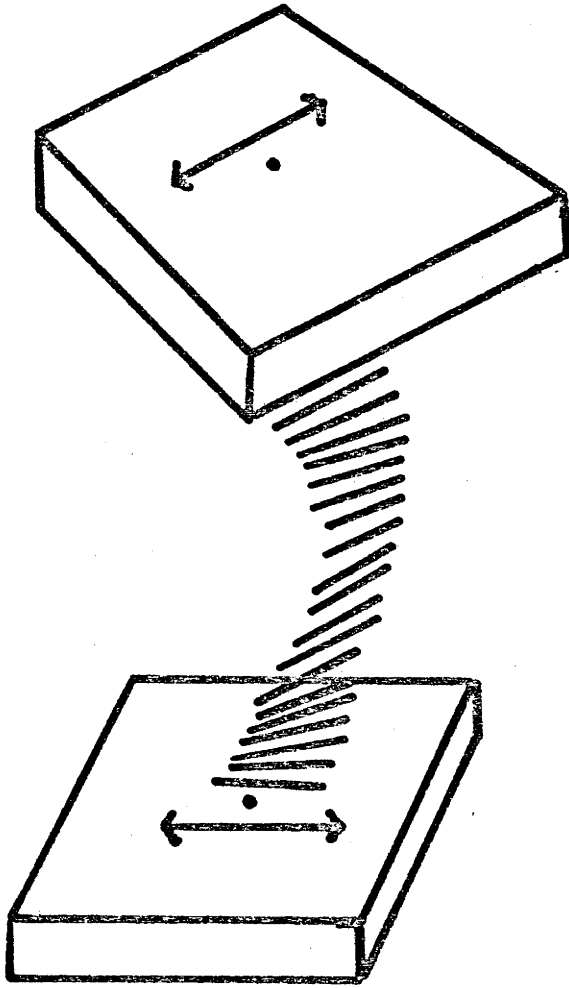
Fig. 1.15 Arrangement of molecules in an isotropic phase at a temperature much greater than  $T_c$

The fact that the isotropic phase does not exhibit a preferred direction over a macroscopic length scale can be explained in terms of a local director. In Fig. 1.14 this would be  $\hat{n}$ . It is postulated that in both the isotropic and nematic phases the local director meanders through the liquid. In the isotropic phase, this meandering would have no long-range correlation whereas in the nematic phase it would favour a direction parallel to the bulk director.

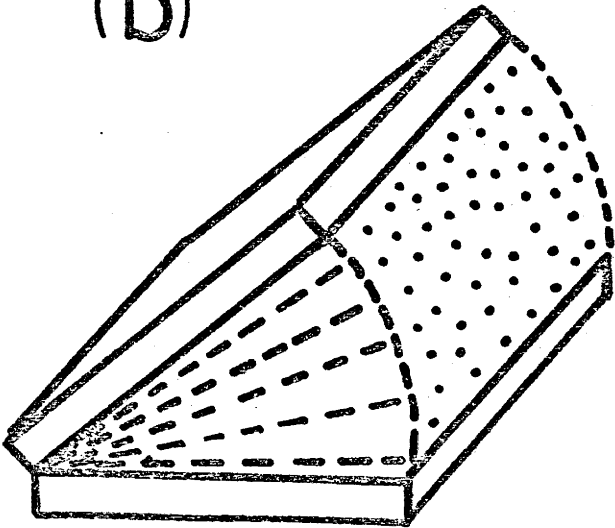
In Chapter 7, a general theory for the isotropic - nematic transition is developed using the direct correlation function  $c(1,2)$ . The direct correlation function would include the effects of both the short ranged repulsions and the longer range attractions. These have been the centre of attention over recent years. The similarity in the local structure at  $T_c$  in both the isotropic and nematic phases is used to quantify certain terms in the direct correlation function. By assuming that the distribution in a small volume ( $\approx 20$  molecules) about the local director is the same for both phases, one can calculate macroscopic properties in terms of the properties in this small volume.

The theory can be extended to study properties of the nematic phase. One consequence of the long range director of molecules is the anisotropy of macroscopic properties. For example, the refractive index and dielectric tensor are anisotropic. One property that will be studied using the theory is the elastic behaviour of the nematic phases. Stresses applied to the nematic phase could result in splaying, twisting and bending of the director. (See Fig. 1.16).

(a)



(b)



(c)

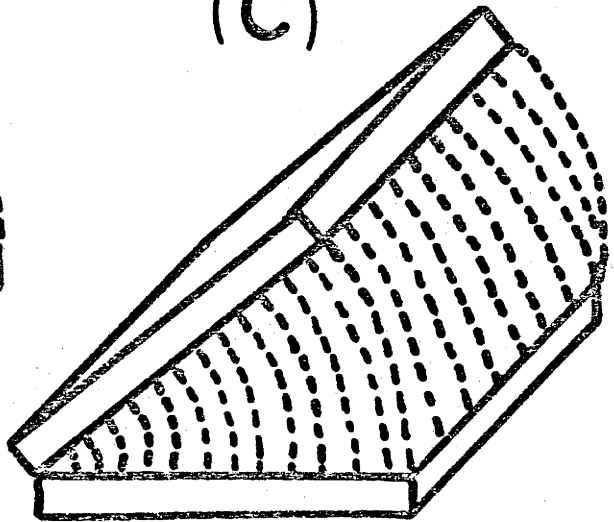


Fig. 1.16 Distortions of nematic liquid crystal: (a) Twisting  
(b) Splaying (c) Bending



This behaviour is characterised by the elastic constants  $K_i$ . The  $K_i$  are calculated in terms of the direct correlation function.

Moreover, the theory will be used to study the behaviour of the nematic phase near a wall. The wall can have the effect of ordering the molecules. In the past this has led to a number of birefringence studies and theoretical studies for the fluid near the single wall. The above theory applied to the system of two walls between which there is a nematic liquid crystal.

#### References

- [1] Patey, G.N., Levesque, D., Weis, J.J., 1979, Molec. Phys., 38, 1635.
- [2] Verwey, E.J.W., Overbeek, J.Th.G., 1948, 'Stability of Lyophobic Colloids', Elsevier Publishing Co.

## CHAPTER 2

## SYMMETRY AND THE ORNSTEIN-ZERNIKE EQUATION

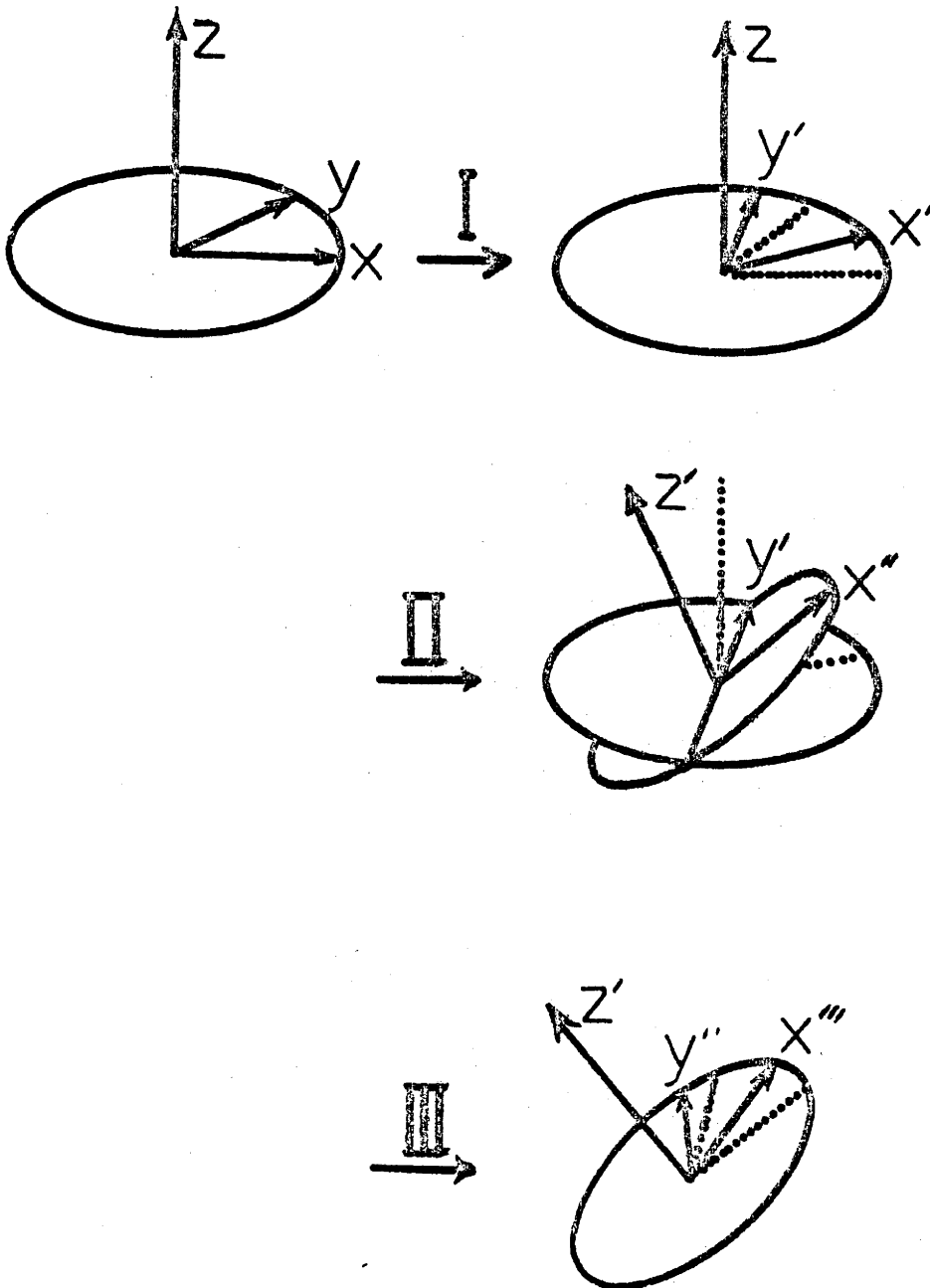
2.1 Rotational Invariant

The main problem in dealing with molecules that interact via anisotropic potentials is to find an adequate yet simple description of the angular dependence. In general, 3 Euler angles are needed to specify the orientation of a molecule — to describe the axis of the molecule (polar and azimuthal angles) and another to specify the rotation about that axis. The interaction potential depends not only on the orientation of both molecules but also on the orientation of the intermolecular axis. To deal with the 3 Euler angles, a generalised spherical harmonic called the Wigner D-function is used. It describes the 3 angles in much the same way as a spherical harmonic does with 2 angles. In the case where there is no dependence on one of the angles the Wigner D-function is proportional to the spherical harmonic. The general properties are listed in Appendix 2-1.

The interaction potential can be written

$$u(1,2) = \sum_{\substack{m_1 n_1 \ell_1 \\ m_2 n_2 \ell_2 \\ m_3 n_3 \ell_3}} u \sum_{\substack{m_1 \\ m_2 m_3}} \sum_{\substack{n_1 \\ n_2 n_3}} \sum_{\substack{\ell_1 \\ \ell_2 \ell_3}} (r) D_{m_2 m_3}^{m_1}(\omega_1) D_{n_2 n_3}^{n_1}(\omega_2) D_{0 \ell_3}^{\ell_1}(\hat{r}) \quad (2.1)$$

Fig. 2.1 Euler angles: I rotation of angle  $\alpha$  about  $z$ -axis  
 II rotation of angle  $\beta$  about  $y'$ -axis  
 III rotation of angle  $\gamma$  about  $z'$ -axis



where  $r$  is the intermolecular separation,  $\omega_1$  is the orientation of molecule 1,  $\omega_2$  is the orientation of molecule 2,  $\hat{r}$  the orientation of the intermolecular axis, all w.r.t. to some laboratory frame  $S$ . Thus  $\omega_1$  represents the 3 Euler angles needed to describe the rotation of the frame  $S$  so that  $S$  lies parallel to 1. Translational invariance has been assumed. Furthermore, the intermolecular potential has rotational invariance. These two invariance properties are the result of the intermolecular potential depending only on the position and orientation of one molecule relative to the other. If the observer, being the origin of a frame of reference, moves to one side or cartwheels, he still sees the same separation and relative orientations and thus the same intermolecular potential. To invoke rotational invariance one writes the potential as seen from some reference frame  $T$  which results from the original frame  $S$  being rotated. Since the potential as seen from frame  $S$  is the same as the one seen from frame  $T$ , the potential is independent of the rotation  $T \leftarrow S$ . In Appendix 2.2 it is shown that this implies the potential can be written as

$$u(1,2) = \sum_{\substack{m \ n \ \ell \\ \mu \ \nu}} u_{\mu\nu}^{mn\ell}(r) \phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r}) \quad (2.2)$$

where

$$\phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r}) = \sum_{\mu', \nu', \lambda'} \begin{pmatrix} m & n & \ell \\ -\mu' & \nu' & \lambda' \end{pmatrix} (-)^{\mu'} D_{\mu\mu'}^m(\omega_1) D_{\nu\nu'}^n(\omega_2) D_{0\lambda'}^\ell(\hat{r}) \quad (2.3)$$

and  $\begin{pmatrix} m & n & \ell \\ -\mu & \nu & \lambda \end{pmatrix}$

is a Wigner 3-J symbol. The important properties of the 3-J symbols and the manner in which they limit the range of summations in (2.2) and (2.3) are given in Appendix 2.3 and [1] and [2]. By using the form (2.2) the angular properties of the potential are separated from the  $r$ -dependence. Our definition of the so-called 'rotational invariant'  $\phi_{\mu\nu}^{mn\ell}$  is the same as that in [3] while that of Blum [4-6] (denoted by a caret) is given by

$$\hat{\phi}_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r}) = (-)^{\mu} [(2m+1)(2n+1)]^{1/2} \phi_{-\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r}) \quad (2.4)$$

## 2.2 Other symmetries

There are some further symmetries worth mentioning.

### (i) Permutation of molecules

There is no reason why one molecule should be labelled 1 and not the other; hence

$$u(1,2) = u(2,1) \quad .$$

In terms of the rotational invariants

$$u(1,2) = \sum_{\substack{mn\ell \\ \mu\nu}} u_{\mu\nu}^{mn\ell}(r) \phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r}) \quad (2.5)$$

$$u(2,1) = \sum_{\substack{m'n'\ell' \\ \mu'v'}} u_{\mu'v'}^{m'n'\ell'}(r) \phi_{\mu'v'}^{m'n'\ell'}(\omega_2, \omega_1, -\hat{r}) \quad (2.6)$$

where  $-\hat{r}$  is the orientation of some frame in which the z-axis is anti-parallel to the z-axis of  $\hat{r}$ . This implies

$$u_{\mu v}^{mn\ell}(r) = (-)^{\mu+v+m+n} u_{-\mu -v}^{nm\ell}(r) \quad (2.7)$$

## (ii) Molecular symmetry

Most molecules have obvious symmetry properties and we shall examine the consequences of some of them.

(a) If the molecular properties are symmetric about the z-axis, then there is no dependence on the rotation  $\gamma$  about that axis. This implies

$$f(1,2) = \sum_{\substack{m \ n \ \ell \\ o \ o}} f_{o \ o}^{m \ n \ \ell}(r) \phi_{o \ o}^{m \ n \ \ell}(\omega_1, \omega_2, \hat{r}) \quad (2.8)$$

(b) If molecules have  $C_{2v}$  symmetry (i.e. a 2 fold rotation about the z-axis as well as a reflection symmetry in the x-y and y-z planes) it can be shown [4] that

$$\gamma_{\mu v}^{m \ n \ \ell}(r) = \gamma_{\pm \mu \pm v}^{m \ n \ \ell}(r) \quad \mu, v \text{ even} \quad (2.9)$$

There are further molecular symmetries mentioned by Blum [4] but these **should** be sufficient for our purposes.

(iii) Combined Molecular Symmetry

In (ii), symmetries of the interaction potential arose when changes in a molecule did not alter the molecule's properties. However this is a special class of symmetries since some symmetries involve both molecules. Consider, for example, a particle imbedded with a tetrahedral quadrupole. A rotation of the particle through an angle of  $\pi/2$  about the z-axis is equivalent to changing the sign of the quadrupole moment. If another particle is similarly rotated, its quadrupole moment is also changed. Thus, the rotation of both particles leaves the quadrupole-quadrupole interaction unaltered.

The symmetries involving both particles are more difficult to find.

2.3 Interaction Potential Involving Ions, Dipoles and Quadrupoles

The electrostatic energy of a system of particles with charges and permanent (non-polarizable) moments can be rigorously written as the sum of energies of each pair of particles

$$\text{i.e. } u(1,2,\dots,N) = \sum_{i=1}^N \sum_{j>i} u(i,j) . \quad (2.10)$$

The latter energy  $u(i,j)$  can be written in terms of the charge, dipole moment and quadrupole tensor of particles  $i$  and  $j$ . This could be done using the equations of Chapter 1 to determine the electrical field produced by particle  $i$  and then calculate the electrostatic energy of particle  $2$  lying in this field. Equation (1.3) describing the field produced by a charge distribution is written with respect to

a reference frame associated with that charge distribution. A particularly convenient frame of reference is one in which the molecular z-axis lies parallel to the dipole. Similarly equation (1.11) describing the electrostatic energy of a charge distribution lying in an electric field is written with a frame of reference associated with that charge distribution. Given that  $u(1,2)$  needs to be calculated for arbitrary separations and orientations, changing from one frame of reference to the other is not particularly convenient.

Instead, the interaction of each charge  $q_i$  in particle 1 with each charge  $q_j'$  in particle 2 is summed:

$$u(1,2) = \sum_i \sum_j \frac{q_i q_j'}{|\underline{r}_i - \underline{r}_j'|} \quad (2.11)$$

The dash indicates quantities associated with particle 2. Self-energies have been ignored. The term  $\frac{1}{|\underline{r}_i - \underline{r}_j'|}$  can be written in terms of the separation of the centres of the particles,  $r$ , the orientation  $\omega_i$  of each particle, as well as the orientation of the interparticle axis. The resulting equation [1,2] is

$$u(1,2) = \sum_{\substack{m,n \\ \mu,\nu}} (-)^{m+\mu} \left( \frac{(2\ell+1)!}{(2m)!(2n)!} \right)^{1/2} \frac{Q_m^{-\mu}(\bar{1}) Q_n^{-\nu}(\bar{2})}{r^{\ell+1}} \quad (2.12)$$

$$\Phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r})$$

$$= \sum_{\substack{m,n \\ \mu,\nu}} u_{\mu\nu}^{mn\ell}(r) \Phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r}) \quad (2.13)$$



Here  $\ell = m + n$  and the multipole moment  $\bar{Q}_m^\mu(\bar{I})$  is defined by

$$\bar{Q}_m^\mu(\bar{I}) = \sum_{\alpha} q_{\alpha} \bar{r}_{\mu\alpha}^m D_{0\mu}^m(\omega_1) \quad (2.14)$$

where the co-ordinate of charge  $\alpha$  is  $(\bar{r}_{\alpha}, \bar{\theta}_{\alpha}, \bar{\phi}_{\alpha})$  in the molecular axis system. The relationship between  $\bar{Q}_m^\mu$  and the multipole moments  $Q_m^\mu$  of equations (12.1-18(a)) of [2] is

$$\bar{Q}_m^\mu(\bar{I}) = i^{\mu-|\mu|} \frac{(m-|\mu|)!}{(m+|\mu|)!}^{1/2} Q_m^\mu(\bar{I}) \quad (2.15)$$

These can be related to the total charge, dipole moment and quadrupole moment using (12.1.16), (12.1.22)-(12.1.24) of [2]. For example  $\bar{Q}_0^0 = q$  is the net charge on the molecule; and if the molecule has a dipole moment,  $\mu$ , along the z-axis;  $\bar{Q}_1^0 = \mu$ .

The symmetries discussed in section 2.2 give us information about the coefficients  $u_{\mu\nu}^{mn\ell}(r)$ . For dipoles, linear quadrupoles or any axisymmetric molecule,  $\mu = \nu = 0$ . For molecules with  $C_{2v}$  symmetry such as water and tetrahedral quadrupoles, we need only  $\mu, \nu = -2, 0, 2$  and

$$u_{\mu\nu}^{mn\ell}(r) = u_{\pm\mu\pm\nu}^{mn\ell}(r) \quad (2.16)$$

If we are dealing with a linear quadrupole, the only non-zero multipole moment in (2.12) are  $\bar{Q}_0^0 = q$  the net charge,  $\bar{Q}_1^0 = \mu$  the dipole moment and  $\bar{Q}_2^0 = \theta_{zz} = -\theta_L$  the linear quadrupole moment <sup>interactions</sup> (cf 1-9). Explicit expressions for the multipole <sub>are</sub>

charge-charge

$$U_{cc} = q^2 \Phi_{00}^{000}(\omega_1, \omega_2, \hat{r}) r^{-1} = q^2 r^{-1}, \quad (2.17)$$

charge-dipole

$$U_{CD} = 3^{1/2} q \mu \Phi_{00}^{011}(\omega_1, \omega_2, \hat{r}) r^{-2}, \quad (2.18)$$

dipole-dipole

$$U_{DD} = -30^{1/2} \mu^2 \Phi_{00}^{112}(\omega_1, \omega_2, \hat{r}) r^{-3}, \quad (2.19)$$

charge-quadrupole

$$U_{CQ_L} = 5^{1/2} q \Theta_L \Phi_{00}^{022}(\omega_1, \omega_2, \hat{r}) r^{-3}, \quad (2.20)$$

dipole-quadrupole

$$U_{DQ_L} = -105^{1/2} \mu \Theta_L \Phi_{00}^{123}(\omega_1, \omega_2, \hat{r}) r^{-4}, \quad (2.21)$$

quadrupole-quadrupole

$$U_{Q_L Q_L} = 3(70)^{1/2} \Theta_L^2 \Phi_{00}^{224}(\omega_1, \omega_2, \hat{r}) r^{-5}, \quad (2.22)$$

In (2.18) and (2.20) the position vector  $r$  is directed towards the higher multipole. We note that for this ion-dipole-linear quadrupole system the molecules have axial symmetry so we always have

$$\mu = 0 = v.$$

If instead of a linear quadrupole, the charge distribution has a tetrahedral quadrupole

$$\hat{\Theta} = \begin{pmatrix} \Theta_T & 0 & 0 \\ 0 & -\Theta_T & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2.23)$$

the non-zero multipole moments are  $\bar{Q}_0^0 = q$ ,  $\bar{Q}_1^0 = \mu$  and

$$\bar{Q}_2^{\pm 2} = (24)^{-1/2} Q_2^{\pm 2} = \left(\frac{2}{3}\right)^{1/2} \Theta_T \quad (2.24)$$

Consequently the charge-charge, charge-dipole and dipole-dipole interactions for this case is the same as that given by (2.17) - (2.19). Interactions involving the tetrahedral quadrupole are of the form

charge-quadrupole

$$U_{CQ_T} = (10/3)^{1/2} q \Theta_T \Phi^{022}(\underline{\omega}_1, \underline{\omega}_2, \hat{r}) r^{-3}, \quad (2.25)$$

dipole-quadrupole

$$U_{DQ_T} = -70^{1/2} \mu \Theta_T \Phi^{123}(\underline{\omega}_1, \underline{\omega}_2, \hat{r}) r^{-4}, \quad (2.26)$$

quadrupole-quadrupole

$$U_{Q_T Q_T} = 2(70)^{1/2} \Theta_T^2 \Phi^{224}(\underline{\omega}_1, \underline{\omega}_2, \hat{r}) r^{-5}, \quad (2.27)$$

with

$$\Phi^{022} \equiv \Phi_{0-2}^{022} + \Phi_{02}^{022}, \quad (2.28)$$

$$\Phi^{123} \equiv \Phi_{0-2}^{123} + \Phi_{02}^{123}, \quad (2.29)$$

$$\Phi^{224} \equiv \Phi_{22}^{224} + \Phi_{-22}^{224} + \Phi_{2-2}^{224} + \Phi_{-2-2}^{224}. \quad (2.30)$$

Thus by comparing (2.20)-(2.22) with (2.25)-(2.27) we see that the potentials involving the tetrahedral quadrupole can be obtained from those for the linear quadrupole by the substitution

$$\begin{aligned} \Theta_L &\rightarrow \left(\frac{2}{3}\right)^{1/2} \Theta_T, \\ \Phi_{00\ mn1} &\rightarrow \Phi^{mn1}. \end{aligned} \quad (2.31)$$

#### 2.4 Ornstein-Zernike

As yet, the method of calculating the correlation function from the interaction energy has not been described. In this thesis, this will be done using integral equation techniques. The development of the integral equation techniques is not given here, but may be found in any of the books on the subject [10-12]. For a potential of the form (2.10) it is found that

$$h(1,2) = c(1,2) + \int \rho(3) c(1,3) h(3,2) d3/8\pi^2 \quad (2.32)$$

and

$$\begin{aligned} \ln(1 + h(1,2)) &= h(1,2) - c(1,2) - \beta u(1,2) + B(1,2) \\ \beta &= 1/kT \end{aligned} \quad (2.33)$$

Here  $h(1,2)$  ( $\equiv g(1,2) - 1$ ) is called the indirect correlation function;  $c(1,2)$  the direct correlation function and  $B(1,2)$  the sum of the bridge diagrams. Both  $c$  and  $B$  are defined by the sum of

certain integrals. Equation (2.32) is called the Ornstein-Zernike (OZ) equation and (2.33) its closure. For hard particles these need to be supplemented by the equation

$$h(1,2) = -1 \quad (2.34)$$

for all separations and orientations in which particles 1 and 2 overlap. For hard spheres of diameter  $R$  this becomes

$$h(1,2) = -1 \quad \text{for } r < R \quad (2.35)$$

There are a number of well known approximations to the closure (2.33).

(i) Hypernetted Chain Approximation (HNC):

$$B(1,2) = 0 \quad (2.36)$$

or

$$\ln(1 + h(1,2)) = h(1,2) - c(1,2) - \beta u(1,2) \quad (2.37)$$

(ii) Percus Yevick (PY):

$$c(1,2) = -(1 - \exp(\beta u(1,2))) (1 + h(1,2)) \quad (2.38)$$

(iii) Mean Spherical Approximation (MSA):

$$c(1,2) = - \beta u(1,2) \quad (2.39)$$

The MSA and PY closures may be regarded as linearised forms of the HNC.

2.5 Correlation functions in an isotropic system

For an isotropic system the correlation functions (g,h,c) will have the same symmetries as the potential. By appealing to translational and rotational invariance of the the bulk fluid, we can use the following expansion

$$f(1,2) = \sum f_{\mu\nu}^{mn\ell}(r) \phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r}) \quad (2.40)$$

where  $f = g, h, c$ . For axisymmetric potentials, only  $f_{00}^{mn\ell}(r)$  are non-zero, whereas in molecules with  $C_{2v}$  symmetry,  $\mu = \nu = -2, 0, 2$  and

$$f_{\mu\nu}^{mn\ell}(r) = f_{\pm\mu\pm\nu}^{mn\ell}(r) \quad (2.41)$$

For molecules with tetrahedral symmetry (e.g. tetrahedral quadrupoles) there is a further symmetry:  $f(1,2)$  is invariant under the rotation of both molecules by  $\pi/2$  about the z-axis of the molecular frame. For tetrahedral quadrupoles, this is equivalent to reversing the sign of each charge. This symmetry implies  $(\mu + \nu) = -4, 0, +4$ . The only coefficients in (2.40) to survive

are  $f_{00}^{mn1}(r)$  and  $f_{\pm 2 \pm 2}^{mn1}(r)$ . Thus, symmetry can reduce the number of coefficients which we need to solve. The problem is to write the O-Z equation and associated closures in terms of  $f_{\mu\nu}^{mn1}(r)$  and solve for these functions. The O-Z equation takes the form of a convolution of the variables  $r_1 - r_2$ ,  $r_2 - r_3$ ,  $r_3 - r_1$ ; so that by taking the three dimensional Fourier transforms it can be written as

$$\tilde{h}(1,2) = \tilde{c}(1,2) + \frac{1}{8\pi^2} \int d\omega_3 \tilde{c}(1,3) \rho \tilde{h}(3,2) \quad (2.42)$$

where

$$\tilde{h}(1,2) = \sum_{\substack{m,n,\ell \\ \mu,\nu}} \tilde{h}_{\mu\nu}^{mn\ell}(k) \phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{k}) \quad (2.43)$$

$$\tilde{h}_{\mu\nu}^{mn\ell}(k) = 4\pi i^\ell \int_0^\rho dr r^2 j_\ell(kr) h_{\mu\nu}^{mn\ell}(r) \quad (2.44)$$

and  $j_\ell(kr)$  is a spherical Bessel function of order  $\ell$  (see Appendix 2.4). There is also a similar set of transformations for  $c$ . We can construct a multiplication table for the angular convolution in (2.24) using the result

$$\begin{aligned} & \frac{1}{8\pi^2} \int d\omega_3 \phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_3, \hat{k}) \phi_{\mu'\nu'}^{m'n'\ell'}(\omega_3, \omega_2, \hat{k}) \\ &= \delta_{nm} \delta_{\mu'\nu'} (-)^{m+n+n'} \sum_L \left( \frac{2L+1}{2n+1} \right) \begin{pmatrix} 1' & \ell & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1' & \ell & L \\ m & n' & n \end{Bmatrix} \phi_{\mu\nu}^{mn'L}(\omega_1, \omega_3, \hat{k}) \end{aligned} \quad (2.45)$$

The range of the sum over  $L$  is limited by the properties of the Wigner 6-J symbol

$$\left\{ \begin{matrix} 1' & \ell & L \\ m & n' & n \end{matrix} \right\}$$

summarized in Appendix 2.3. We substitute (2.42) into (2.43) and use (2.45) together with the orthogonality condition (see Appendix 2.1)

$$\begin{aligned} & \frac{1}{(8\pi)^{2/3}} \int d\omega_1 \int d\omega_2 \int d\hat{k} \phi_{\mu\nu}^{mn\ell*}(\omega_1, \omega_2, \hat{k}) \phi_{\mu'\nu'}^{m'n'\ell'}(\omega_1, \omega_2, \hat{k}) \\ &= \frac{1}{(2m+1)(2n+1)(2\ell+1)} \delta_{mm'} \delta_{\mu\mu'} \delta_{\nu\nu'} \delta_{\ell\ell'} \end{aligned} \quad (2.46)$$

to obtain

$$\begin{aligned} \hat{h}_{\mu\nu}^{mn\ell}(k) &= \hat{c}_{\mu\nu}^{mn\ell}(k) + \sum_{n'1'1''v'} (-)^{m+n+n'} \begin{pmatrix} 1'' & 1' & \ell \\ 0 & 0 & 0 \end{pmatrix} \\ & \left\{ \begin{matrix} 1'' & 1' & \ell \\ m & n & n' \end{matrix} \right\} \left( \frac{2\ell+1}{2n'+1} \right) \hat{c}_{\mu\nu}^{mn'1'}(k) \rho \hat{h}_{v'v}^{n'n1''}(k) \\ & \quad |v'| \leq n' \end{aligned} \quad (2.47)$$

which is equivalent to equations (2.18)-(2.21) of [5]. Following Blum [4] we define the linear combinations (see Appendix 2-4)

$$\tilde{f}_{x,\mu\nu}^{mn}(k) = (-)^x \sum_{\ell} \begin{pmatrix} m & n & \ell \\ x & x & 0 \end{pmatrix} \tilde{f}_{\mu\nu}^{mn\ell}(k) \quad (2.48)$$

and use the properties of the 6-J symbol to get

$$\tilde{h}_{x,\mu\nu}^{mn}(k) = \tilde{c}_{x,\mu\nu}^{mn}(k) + \sum_{n'1'v'} \frac{1}{2n'+1} \tilde{c}_{x,\mu\nu'}^{mn'}(k) \rho \tilde{h}_{x,v'v}^{n'n} \quad (2.49)$$



where  $n' \geq x$  and  $|v'| \leq n'$ . Equation (2.49) which is equivalent to equation (2.33) of [4], is a general result which resembles the O-Z equation for a simple fluid mixture since all angular variables have been removed and the functions depend only on the magnitude of the wave vector.

The transformation in (2.48) is a generalisation of Wertheim's choice of  $h^+$  and  $h^-$  as a linear combination of  $h^\Delta$  and  $h^D$  for the case of dipolar fluids [7]. For each allowed value of  $x$ , (2.49) separates into a series of simpler equations of the usual O-Z forms with block matrix structure. The above equations can be generalised in the usual way for mixtures.

## 2.6 Cylindrical Symmetry

The correlation functions need not always have the same symmetries as the interaction potential. While the interaction potential only depends on the relative positions and orientations of the molecules, the same is not always true of the correlation functions. Consider, for example, an 'aligned' fluid (i.e. a fluid in which the molecules have a preferred orientation). Two such fluids would be

- (i) a system of dipoles under the influence of an external field  $\underline{E}$ .
- (ii) a nematic liquid crystal.

In (i) the dipoles tend to align parallel to  $\underline{E}$  and in (ii) the molecules tend to align parallel to the direction  $\hat{r}$ . There is a major difference between the examples. In (i) almost no particles

lie anti-parallel to  $\underline{E}$  whereas in (ii) there is no distinction between  $\hat{\underline{r}}$  and  $-\hat{\underline{r}}$ .

The correlation functions of an aligned fluid depend not only on the orientations of the molecules relative to each other, but also their position and orientation relative to the preferred direction. (This direction shall hereafter be referred to as the 'principal axis'.) Thus these correlation functions still have translational invariance but the rotational invariance has been replaced by a more restricting condition. Whereas the interaction potential is unaffected by the rotation of the frame of reference about any axis, the correlation functions are generally affected by all rotations except those about an axis parallel to the principal axis. In Appendix 2.5 it is shown that the correlation functions can be written (for cylindrically symmetric particles)

$$f(1,2) = \sum f_{\mu\nu}^{mn\ell}(\underline{r}) \psi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{\underline{r}}, \hat{\underline{z}}) \quad (2.50)$$

$$\psi_{\mu\nu}^{mn\ell}(1,2, \hat{\underline{R}}, S) = D_{o\mu}^m(\omega_1) D_{o\nu}^n(\omega_2) D_{o\lambda}^{\ell}(\hat{\underline{r}}) \delta_{\lambda, \mu - \nu} \quad (2.51)$$

measured w.r.t. a frame S, in which the z-axis is parallel to the principle axis. This result is a simple consequence of rotating the frame of reference about the principle axis. In the case of rotational symmetry, the coefficient degenerates into the following form

$$f_{\mu\nu}^{mn\ell}(\underline{r}) = f_{o0}^{mn\ell} \begin{pmatrix} m & n & 1 \\ -\mu & \nu & \lambda \end{pmatrix} (-)^{\mu} \quad (2.52)$$

where the notation on the r.h.s. is the same as eqn. (2.2).

## 2.7 Symmetry of dipoles in an external field

A system of dipoles under the influence of an external field  $\underline{E}$  is an example of an 'aligned' fluid. Therefore, its correlation functions  $f(1,2)$  ( $f = g, h, c$ ) can be written

$$f(1,2) = \sum f_{\mu\nu}^{mn\ell}(r) \psi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r}, \hat{z}) \quad .$$

Clearly  $f(1,2)$  remains invariant under the permutation of molecules and so

$$h_{\mu\nu}^{mn\ell}(r) = (-)^{\mu+\nu+\ell} h_{-\nu-\mu}^{mn\ell}(r) \quad (2.53)$$

There is another symmetry which is not so obvious. Consider the dipoles in Fig. 2.2. The centres lie in the plane of the page (x-z plane) and generally their axes lie out of the plane. If both molecules are reflected about the x-z plane

- |       |                                             |                  |
|-------|---------------------------------------------|------------------|
| (i)   | $\underline{\mu} \cdot \underline{E}$       | remains constant |
| (ii)  | $\underline{\mu}_1 \cdot \underline{\mu}_2$ | remains constant |
| (iii) | $\underline{\mu} \cdot \hat{r}$             | remains constant |

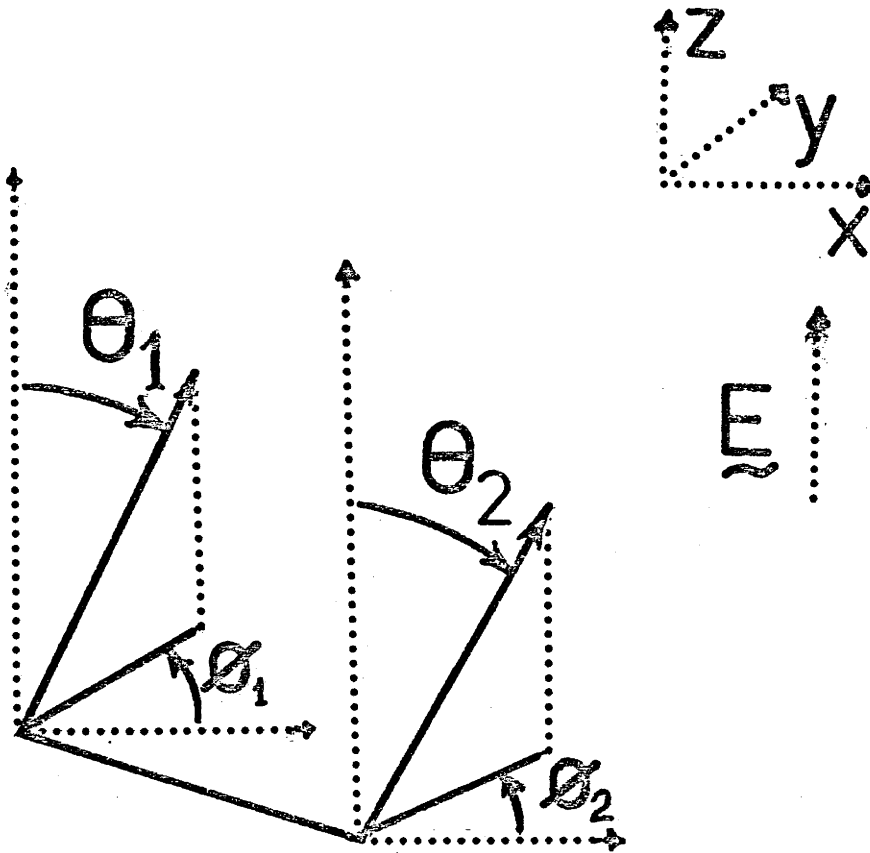


Fig. 2.2 Two dipoles in an external Field  $\vec{E}$ .

The correlation function should therefore be invariant under this reflection. Thus

$$h_{\mu\nu}^{mnl}(r) = h_{-\mu-\nu}^{mnl}(r) \quad (2.54)$$

## 2.8 0-Z equation for cylindrically symmetric systems

If it exists, the 3-dimensional Fourier transform  $\tilde{f}$  of a cylindrically invariant function  $f$  takes the form

$$\tilde{f} = \sum \tilde{f}_{m'n'}^{mn\ell}(k) \psi_{m'n'}^{mn\ell}(\omega_1, \omega_2, \hat{k}, \hat{z}) \quad (2.55)$$

where

$$\tilde{f}_{m'n'}^{mn\ell}(k) = 4\pi(i)^\ell \int_0^\infty dr r^2 j_\ell(kr) f_{m'n'}^{mn\ell}(r) \quad (2.56)$$

In terms of this Fourier transform, the 0-Z equation for a cylindrically symmetric system becomes

$$\tilde{h}_{v\mu}^{mn\ell}(k) = \tilde{c}_{v\mu}^{mn\ell}(k) + \sum_{p=0} \sum_{r' \mu' p_1' \atop 1'' m'} \rho_{r' \mu' p_1'} \tilde{c}_{v\mu}^{mn' \ell'}(k) \tilde{h}_{\mu' \mu}^{m' n' \ell''}(k) \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \quad (2.57)$$

$$\begin{pmatrix} 1' & 1'' & \ell \\ \lambda' & \lambda'' & -\lambda \end{pmatrix} (2\ell + 1) \begin{pmatrix} p & n' & m' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} p & n' & m' \\ 0 & \mu' & -\mu' \end{pmatrix} (-)^{\lambda + \mu'}$$

where the density

$$\rho(\omega) = \sum_{p=0}^{\infty} \rho_p P_p(\cos \theta) \quad (2.58)$$

where  $\theta$  is the second Euler angle of  $\omega$ .

The expression (2.57) is too complicated to be useful. It is only for special cases where the density expansion (2.58) is simple that these equations degenerate into useful forms. For instance, the equations here must agree with the results for the isotropic system

as given by (2.47). In Appendix 2-6 it is shown to be true and

$$h_{\mu\nu}^{mn\ell}(r) = (-)^v \begin{pmatrix} m & n & \ell \\ -\mu & \nu & \lambda \end{pmatrix} h_{oo}^{mn\ell}(r) \quad (2.59)$$

where the LHS is the coefficient of  $\psi_{\mu\nu}^{mn\ell}$  and the RHS is the coefficient of  $\phi_{oo}^{mn\ell}$ .

Another special case is a system of totally aligned molecules. In Appendix (2.6) it is shown that the equations (2.57) reduce to

$$\tilde{h}_\ell(k) = c_\ell(k) + \sum_{1'1''} \rho \begin{pmatrix} 1' & 1'' & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \tilde{c}^{1'}(k) \tilde{h}^{1''}(k) (2\ell + 1) \quad (2.60)$$

where

$$h(1,2) = \sum_\ell h_\ell(r) P_\ell(\cos\theta) \quad (2.61)$$

This agrees with another derivation [13].

## 2.9 Summary

The angular dependence of the interaction potential and the correlation functions anions can be contained in a set of orthogonal functions. For all the systems described, the interaction energy can be written

$$u(1,2) = \sum u_{\mu\nu}^{mn\ell}(r) \phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r})$$

The coefficient depends only on the intermolecular separation and  $\phi_{\mu\nu}^{mn\ell}$  only on the orientations  $\omega_1, \omega_2$  and  $\hat{r}$ . Similarly, the

correlation functions  $f(1,2)$  ( $f = g, h, c$ ) can be written

$$f(1,2) = \sum f_{\mu\nu}^{mn\ell}(r) \phi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r})$$

for an isotropic system and

$$f(1,2) = \sum f_{\mu\nu}^{mn\ell}(r) \psi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{r}, \hat{z})$$

for an aligned system.

The problem is to calculate the coefficients  $f_{\mu\nu}^{mn\ell}(r)$  from the functions  $u_{\mu\nu}^{mn\ell}(r)$ . This is done with the use of the Ornstein-Zernike (O-Z) equation. The O-Z equation has been written in terms of  $f_{\mu\nu}^{mn\ell}(r)$  in (2.49) for the bulk systems and in (2.57) for the aligned system. There are an infinite number of coefficients  $f_{\mu\nu}^{mn\ell}(r)$  and some truncation needs to be made.

The O-Z equation is supplemented by the closure relation. Apart from the MSA which is expected to be inaccurate, the closures are nonlinear functions of the correlation functions and the interaction potential and hence the orthogonal functions  $\phi$  and  $\psi$ . These need to be either expanded in the  $\phi$ 's and  $\psi$ 's and approximated. The closure relation will be discussed in detail in the work on dipoles.

The symmetry properties are very useful in reducing the number of equations. In particular, the work on the tetrahedral quadrupole is simplified by its symmetry properties.

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## Appendix 2.1 Wigner-D Functions

The generalized spherical harmonic  $D_{mn}^{\ell}(\omega)$  can be written as

$$D_{mn}^{\ell}(\omega) = \exp(in\gamma) d_{nm}^{\ell}(\cos\beta) \exp(im\alpha) \quad (A1)$$

where  $(\alpha, \beta, \gamma)$  are the Euler angles (cf. Fig. 2.1). (A1) denotes the index-to-angle convention of [2]. Edmonds [1] has a different convention but this makes little practical difference.  $d_{nm}^{\ell}(\cos\theta)$  can be written as a Jacobi polynomial [1] but the only properties we need are

$$(1) \quad D_{0m}^{\ell}(\omega) = \left(\frac{4\pi}{2\ell+1}\right)^{1/2} Y_{\ell}^m(\theta, \phi) \quad (A2)$$

$$= i^{|m|} |m|^{-m} \left(\frac{(\ell-|m|)!}{(\ell+|m|)!}\right)^{1/2} P_{\ell}^m(\cos\theta) \times \exp(im\phi) \quad (A3)$$

where  $P_{\ell}^m(\cos\theta)$  is an associated Legendre function and  $Y_{\ell}^m(\theta, \phi)$  is a spherical harmonic.

$$(2) \quad D_{mn}^{\ell*}(\omega) = (-1)^{n-m} D_{-n-m}^{\ell}(\omega) \quad (A4)$$

$$(3) \quad D_{mn}^{\ell}(\omega) D_{m_1 n_1}^{\ell_1}(\omega) = \sum_{LMN} (2L+1) D_{MN}^L(\omega) \quad (A5)$$

$$(4) \quad \sum_{m, n} D_{mn}^{\ell}(\omega) D_{m_1 n_1}^{\ell_1}(\omega) \begin{pmatrix} \ell & l_1 & L \\ m & m_1 & M \end{pmatrix} \begin{pmatrix} \ell & l_1 & L \\ n & n_1 & N \end{pmatrix} \\ = \frac{\delta_{LL'}}{2L+1} D_{MN}^{L''}(\omega) \quad (A6)$$

$$(5) \quad \frac{2\ell + 1}{8\pi^2} \int d\omega D_{mn}^{\ell}(\omega) D_{m_1 n_1}^{\ell_1}(\omega) = \delta_{mm_1} \delta_{nn_1} \delta_{\ell\ell_1}$$

$$(6) \quad \frac{1}{8\pi^2} \int d\omega D_{m_1 n_1}^{l_1}(\omega) D_{m_2 n_2}^{l_2}(\omega) D_{m_3 n_3}^{l_3}(\omega) \\ = \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ n_1 & n_2 & n_3 \end{pmatrix} \quad (A7)$$

$$(7) \quad D_{mn}^{\ell}(\omega_1) = \sum_{n'} D_{mn'}^{\ell}(\omega_2) D_{n'm}^{\ell}(\omega_3) \quad (A8)$$

where  $\omega_1$  is the result of the 2 rotations  $\omega_2, \omega_3$ .

## Appendix 2.2 Rotational Invariants

Relative to a frame S the potential  $u(1,2)$  can be written

$$u(1,2) = \sum_{\substack{m_1 n_1 l_1 \\ m_2 n_2 l_2 \\ m_3 n_3 l_3}} u \begin{pmatrix} m_1 n_1 l_1 \\ m_2 n_2 l_2 \\ m_3 n_3 l_3 \end{pmatrix} (r) D_{m_2 m_3}^{m_1}(\omega_1) D_{n_2 n_3}^{n_1}(\omega_2) D_{l_2 l_3}^{l_1}(\hat{R}) \quad (B1)$$

Suppose that relative to a frame T the orientations of molecules, 1,2 and the intermolecular axis are  $\omega_3, \omega_4, \hat{p}$  and that the rotation  $S \rightarrow T$  is given by  $\omega_5$ . Using (A8)

$$D_{n_2 m_3}^{m_1}(\omega_1) = \sum_{m_4} D_{m_2 m_4}^{m_1}(\omega_3) D_{m_4 m_3}^{m_1}(\omega_5) \quad (B2)$$

Similarly for  $D_{n_2 n_3}^{n_1}(\omega_2)$ ,  $D_{l_2 l_3}^{l_1}(\hat{R})$ . Using the multiplication rule (A5) on all rotations of  $\omega_5$ , one obtains the following equation

$$u(1,2) = \sum_{m_1 n_1 l_1} \sum_{\substack{LMF \\ DEF}} u_{m_2 n_2 l_2}^{m_1 n_1 l_1}(r) D_{m_2 m_4}^{m_1}(\omega_3)$$

$$D_{n_2 n_4}^{n_1}(\omega_4) D_{l_2 l_4}^{l_1}(\hat{P}) \times \begin{pmatrix} m_1 & n_1 & L \\ m_4 & n_4 & M \end{pmatrix} \begin{pmatrix} m_1 & n_1 & L \\ m_2 & n_2 & N \end{pmatrix} \begin{pmatrix} L & l_1 & D \\ -N & l_2 & E \end{pmatrix}$$

$$(2L + 1) \begin{pmatrix} L & l_1 & D \\ -M & l_3 & F \end{pmatrix} (2D + 1) D_{EF}^D(\omega_5) (-)^{M+N} \quad (B3)$$

Since the potential is independent of the rotation  $T \rightarrow S$

$$D = E = F = 0 \quad (B4)$$

$$m = l_4 \quad N = l_3 \quad L = l_1 \quad (B5)$$

By writing

$$u_{m_2 n_2}^{m_1 n_1 l_1} = \sum_{m_3 n_3 l_3} u_{-m_2 n_2 l_2}^{m_1 n_1 l_1}(r) (-)^{m_2} \begin{pmatrix} m_1 n_1 l_1 \\ m_3 n_3 l_3 \end{pmatrix} \quad (B6)$$

one finds that

$$u(1,2) = \sum_{\substack{m_1 n_1 l_1 \\ m_2 n_2}} u_{m_2 n_2}^{m_1 n_1 l_1}(r) \phi_{m_2 n_2}^{m_1 n_1 l_1}(\omega_3, \omega_4, \hat{r}) \quad (B7)$$

$$\begin{aligned} \Phi_{m_2 n_2}^{m_1 n_1 l_1}(\omega_1, \omega_2, \hat{R}) &= \sum_{\mu, \nu} \begin{pmatrix} m_1 n_1 l_1 \\ -\mu \nu \lambda \end{pmatrix} (-)^{\mu} \\ & D_{m_2 \mu}^{m_1}(\omega_1) D_{n_2 \nu}^{n_1}(\omega_2) D_{0 \lambda}^{l_1}(\hat{R}) \end{aligned} \quad (B8)$$

### Appendix 2.3      3-J and 6-J Symbols

The Wigner 3-j and 6-j symbols are discussed and tabulated in Rotenberg et al [8]. The useful properties of the 3-j are the following:

$$(1) \quad \begin{pmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{pmatrix} = 0 \quad \text{if } m_i > j_i \text{ for any } i \quad (C1)$$

$$(2) \quad \begin{pmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{pmatrix} = 0 \quad \text{unless } m_1 + m_2 + m_3 = 0 \quad (C2)$$

$$(3) \quad \begin{pmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{pmatrix} = \begin{pmatrix} j_k j_l j_n \\ m_k m_l m_n \end{pmatrix} \quad \text{if } (kln) \text{ is an even permutation of } (123) \quad (C3)$$

$$= (-)^{j_1+j_2+j_3} \begin{pmatrix} j_k j_l j_n \\ m_k m_l m_n \end{pmatrix} \quad \text{if } (kln) \text{ is an odd permutation of } (123) \quad (C4)$$

$$= (-)^{j_1+j_2+j_3} \begin{pmatrix} j_1 j_2 j_3 \\ -m_1 -m_2 -m_3 \end{pmatrix} \quad (C5)$$

$$(4) \quad \begin{pmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{pmatrix} = 0 \quad \text{unless } j_k + j_l > j_n > |j_k - j_l| \quad (C6)$$

for any permutation of  $(kln)$ , i.e. unless  $(j_1 j_2 j_3)$  satisfy the triangle inequality.

(5) Orthogonality Conditions

$$\sum_{j_3 m_3} (2j_3 + 1) \begin{pmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{pmatrix} \begin{pmatrix} j_1 j_2 j_3 \\ m_1' m_2' m_3 \end{pmatrix} = \delta_{m_1 m_1'} \delta_{m_2 m_2'} \quad (C7)$$

and

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{pmatrix} \begin{pmatrix} j_1 j_2 j_3' \\ m_1 m_2 m_3' \end{pmatrix} = \frac{1}{2j_3 + 1} \delta_{j_3 j_3'} \delta_{m_3 m_3'} \quad (C8)$$

The 6-J symbols have the following properties:

$$(1) \quad \left\{ \begin{matrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{matrix} \right\}$$

is invariant under the interchange of columns and under the interchange of any two numbers in the bottom row with the corresponding two numbers in the top row.

$$(2) \quad \left\{ \begin{matrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{matrix} \right\} = 0$$

unless the triplets  $(j_1 j_2 j_3)$ ,  $(m_1 j_2 m_3)$ ,  $(m_1 m_2 j_3)$ ,  $(j_1 m_2 m_3)$  all satisfy the triangle inequality (C6).

$$(3) \quad \sum_{\{n\}} (-1)^S \begin{pmatrix} j_1 l_2 l_3 \\ m_1 n_2 - n_3 \end{pmatrix} \begin{pmatrix} l_1 j_2 l_3 \\ -n_1 m_2 n_3 \end{pmatrix} \begin{pmatrix} l_1 l_2 j_3 \\ n_1 - n_2 m_3 \end{pmatrix} \quad (C9)$$

$$= \begin{pmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{pmatrix} \left\{ \begin{matrix} j_1 j_2 j_3 \\ l_1 l_2 l_3 \end{matrix} \right\}$$

where  $S = l_1 + l_2 + l_3 + n_1 + n_2 + n_3$ .

## Appendix 2.4 Transformations

The various transformations used in this paper and earlier works [4-6,7] are summarized in Fig.A.2 , and the relation between our notation and that of Blum [6] is shown on the table.

We start with the real coefficient functions ( $f = h$  or  $c$ ). On Fourier transforming in three dimensions we get the transform pair

( $\mu$  and  $\nu$  are suppressed in this appendix)

$$f^{mn\ell}(r) = \frac{(-i)^\ell}{2\pi^2} \int_0^\infty dk k^2 j_\ell(kr) \tilde{f}^{mn\ell}(k) \quad , \quad (D.1)$$

$$\tilde{f}^{mn\ell}(k) = 4\pi i^\ell \int_0^\infty dr r^2 j_\ell(kr) f^{mn\ell}(r) \quad .$$

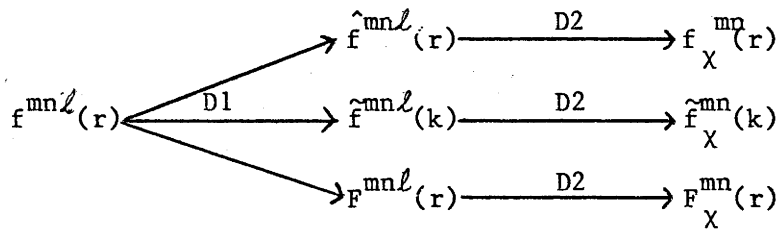


Fig.A.2 Transformation schemes for the coefficient functions in the Ornstein-Zernike equation - indices ( $\mu, \nu$ ) have been suppressed.

Notational difference between this work and Blum [1]

Notation of this paper		Notation of [4]	
$h^{mn\ell}(r)$		$\hat{h}^{mn\ell}(r)$	
$\tilde{h}^{mn\ell}(k)$		$h^{mn\ell}(k)$	
$\hat{h}^{mn\ell}(r)$	o/e	$H^{mn\ell}(r)$	o/e
$\tilde{h}_X^{mn\ell}(k)$		$H_X^{mn\ell}(k)$	
$h_X^{mn\ell}(r)$	o/e	$h_X^{mn\ell}(r)$	o/e
$H_X^{mn\ell}(r)$	o/e	No equivalent	
$H_X^{mn\ell;e}(r) \pm H_X^{mn\ell;o}(r)$		$h_X^{*mn\ell;\pm}(r)$	

We then take the linear combination of  $\tilde{f}^{mn\ell}(k)$  which simplifies the matrix structure of the O-Z equation.

$$\tilde{f}_\chi^{mn}(k) = \sum_{\ell} (-1)^{\chi} \begin{pmatrix} m & n & \ell \\ \chi & -\chi & 0 \end{pmatrix} \tilde{f}^{mn\ell}(k) , \quad (D.2)$$

$$\tilde{f}^{mn\ell}(k) = (2\ell + 1) \sum_{\chi} (-1)^{\chi} \begin{pmatrix} m & n & \ell \\ \chi & -\chi & 0 \end{pmatrix} \tilde{f}_\chi^{mn}(k) .$$

$$\hat{f}^{mn\ell}(r) = \frac{1}{2\pi^2} \int_0^\infty dk k^2 \begin{Bmatrix} j_0(kr) \\ -ij_1(kr) \end{Bmatrix} \tilde{f}^{mn\ell}(k) , \quad (D.3)$$

$$\tilde{f}^{mn\ell}(k) = 4\pi \int_0^\infty dr r^2 \begin{Bmatrix} j_0(kr) \\ ij_1(kr) \end{Bmatrix} \hat{f}^{mn\ell}(r) ,$$

where  $\ell$  is  $\begin{Bmatrix} \text{even} \\ \text{odd} \end{Bmatrix}$ . The chief disadvantage of this method is the need to use different transforms depending on the parity of  $\ell$ . For a dipolar fluid, this complication does not arise and Wertheim [7] introduced  $\hat{f}^{110}(r)$  and  $\hat{f}^{112}(r)$  directly, without passing through Fourier space. (His use of the caret is the origin of our notation for these functions.) They are related to the original functions by

$$\hat{f}^{mn\ell}(r) = \int_0^\infty ds s^2 f^{mn\ell}(s) \theta_\ell(s, r) , \quad (D.4)$$

$$f^{mn\ell}(r) = \int_0^\infty ds s^2 \hat{f}^{mn\ell}(s) \theta_\ell(r, s) ,$$

where

$$\theta_\ell(r, s) \equiv \frac{2}{\pi} i^\ell \int_0^\infty ds k^2 j_\ell(kr) \begin{Bmatrix} j_0(ks) \\ -ij_\ell(ks) \end{Bmatrix}$$

for  $\ell \in \begin{cases} \text{even} \\ \text{odd} \end{cases}$ . A general expression for  $\theta_\ell(r, s)$  is given in [6] and explicit expressions for  $\ell = 2, 4$  in [5].

An alternative route is to follow Baxter [9] and take a one dimensional Fourier transform back to real space

$$\begin{aligned} F^{\text{mn}\ell}(r) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp(-ikr) \hat{f}^{\text{mn}\ell}(k) , \\ \hat{f}^{\text{mn}\ell}(k) &= \int_{-\infty}^{\infty} dr \exp(ikr) F^{\text{mn}\ell}(r) . \end{aligned} \quad (\text{D.5})$$

The advantage of this method is that the distinction between even  $\ell$  and odd  $\ell$  does not arise. These new functions are related to the original ones by

$$\begin{aligned} 2\pi f^{\text{mn}\ell}(r) &= 2\pi \int_{|r|}^{\infty} ds s f^{\text{mn}\ell}(s) P_\ell\left(\frac{r}{s}\right) , \\ &= -\frac{d}{dr} F^{\text{mn}\ell}(r) + \frac{P'_\ell(1)}{r} F^{\text{mn}\ell}(r) \\ &\quad - \frac{1}{r^2} \int_0^r ds P''_\ell\left(\frac{s}{r}\right) F^{\text{mn}\ell}(s) , \end{aligned} \quad (\text{D.6})$$

where  $P_\ell(x)$  is a Legendre polynomial.

The two sets of functions  $F, f$  are in turn related by

$$\begin{aligned} F^{\text{mn}\ell}(r) &= 2\pi \int_{|r|}^{\infty} ds \left\{ \frac{s}{r} \right\} \hat{f}^{\text{mn}\ell}(s) , \\ 2\pi r f^{\text{mn}\ell}(r) &= -\frac{d}{dr} F^{\text{mn}\ell}(r) \quad \text{for } \ell \in \begin{cases} \text{even} \\ \text{odd} \end{cases} \end{aligned} \quad (\text{D.7})$$



For analytical work (viz. the MSA), both sets of functions ( $F$  and  $f$ ) have the necessary properties for solution by Baxter's method [9]. For numerical work, however, the transforms from  $f^{mnl}(r)$  back to  $f^{mnl}(r)$  involves only integrals whereas the transform from  $F^{mnl}(r)$  to  $f^{mnl}(r)$  involves a differentiation. This seems to make the set  $f^{mnl}(r)$  preferable for numerical work.

### Appendix 2.5 Cylindrical Invariants

Consider a frame  $S$ , in which the  $z$ -axis is parallel to the principal axis. With respect to this frame,  $f(1,2)$  may be written

$$f(1,2) = \sum_{\substack{mnl \\ \mu\nu\lambda}} f_{\mu\nu}^{mnl}(r) D_{o\mu}^{*m}(\omega_1) D_{ov}^n(\omega_2) D_{o\lambda}^{\ell}(\hat{R})$$

where  $\omega_1, \omega_2, \hat{R}$  have their usual meaning. Now consider another frame  $T$  which originates from  $S$  being rotated about the  $z$ -axis by an angle  $\alpha'$ . If  $\omega'_1, \omega'_2, \hat{R}'$ , are the new orientations

$$D_{ov}^n(\omega'_2) = D_{ov}^n(\omega_2) e^{i\nu\alpha'} \quad (E.1)$$

Similarly for  $\omega'_1, \hat{R}'$ .

Since  $f(1,2)$  should be independent of such rotations

$$-\mu + \nu + \lambda = 0 \quad (E.2)$$

### Appendix 2.6 Isotropic System and Totally Aligned Systems

For aligned fluid, it is shown [eq. (2.57)] that

$$\tilde{h}_{\nu\mu}^{mn\ell}(k) = \tilde{c}_{\nu\mu}^{mn\ell}(k) + \sum_{p=0} \sum_{\substack{n'\mu'1' \\ l''m'}} \rho_p \tilde{c}_{\nu\mu'}^{mn'l'}(k) \tilde{h}_{\mu'\mu}^{m'n1''}(k) \quad (\text{F.1})$$

$$\begin{pmatrix} 1' & 1'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1' & 1'' & \ell \\ \lambda' & \lambda'' & -\lambda \end{pmatrix} (2\ell + 1) \begin{pmatrix} p & n' & m' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} p & n' & m' \\ 0 & \mu' & -\mu' \end{pmatrix} (-)^{\lambda+\mu'}.$$

The system is characterised by the Legendre expansion of the density

$$\rho(\omega) = \sum_{p=0}^{\infty} \rho_p(\cos\theta) \quad (\text{F.2})$$

For an isotropic system there is no preferred direction and

$$\rho_p = \rho \delta_{p,0} \quad (\text{F.3})$$

In a totally aligned fluid

$$\rho_p = (2p + 1) \cdot \quad (\text{F.4})$$

#### (a) Isotropic System

Substituting (F3) into (F1) and using the triangle inequality

(C6) in Appendix 2.3, we obtain

$$n' = m' \quad (\text{F5})$$

and

$$\tilde{h}_{v\mu}^{mn\ell}(k) = \tilde{c}_{v\mu}^{mn\ell}(k) + \sum_{p=0}^{\infty} \sum_{\substack{n'\mu'1' \\ 1''m'}} \rho \tilde{c}_{v\mu'}^{mn'1'}(k) \quad (\text{F.6})$$

$$\tilde{h}_{\mu'\mu}^{n'nl''}(k) \begin{pmatrix} 1' & 1'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1' & 1'' & \ell \\ \lambda' & \lambda'' & -\lambda \end{pmatrix} (2\ell + 1) (-)^{\lambda+\mu'}.$$

The substitution

$$\tilde{h}_{v\mu}^{mn\ell}(k) \equiv (-)^v \begin{pmatrix} m & n & \ell \\ v & \mu & \lambda \end{pmatrix} \tilde{h}_{v\mu}^{mn\ell}(k) \quad (\text{F.7})$$

yields

$$\begin{aligned} \tilde{h}_{v\mu}^{mn\ell} &= \tilde{c}_{v\mu}^{mn\ell} + \sum_{\substack{n'\mu' \\ 1'1''}} (-)^{n+m+n'} \left\{ \begin{matrix} m & n & \ell \\ 1'' & 1' & n' \end{matrix} \right\} \\ &\begin{pmatrix} 1' & 1'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \tilde{c}_{v\mu'}^{mn'1'} \tilde{h}_{\mu'\mu}^{n'nl''} \frac{\rho}{(2n'+1)} (2\ell + 1). \end{aligned} \quad (\text{F.8})$$

Here the properties of the 6-J symbol have been used (See Appendix 2.3). Equation(F8) is independent of  $v$  and  $\mu$ . Thus we may write

$$\tilde{h}_{v\mu}^{mn\ell}(k) = \tilde{h}^{mn\ell}(k) \delta_{v,0} \delta_{\mu,0}. \quad (\text{F.9})$$

However

$$\phi_{00}^{mn\ell}(\omega_1, \omega_2, \hat{R}) = \sum_{\mu} (-)^{\mu} \begin{pmatrix} m & n & \ell \\ \mu & v & \lambda \end{pmatrix} \psi_{\mu v}^{mn\ell}(\omega_1, \omega_2, \hat{R}, \hat{z})$$

therefore

$$\begin{aligned}
\tilde{h} &= \sum \tilde{h}_{\mu\nu}^{mn\ell}(k) \psi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{k}, \hat{z}) \\
&\quad \sum \begin{pmatrix} m & n & \ell \\ \mu & \nu & \lambda \end{pmatrix} (-)^{\mu} \tilde{h}_{\mu\nu}^{mn\ell}(k) \psi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{k}, \hat{z}) \\
&= \sum \begin{pmatrix} m & n & \ell \\ \mu & \nu & \lambda \end{pmatrix} (-)^{\mu} \tilde{h}^{mn\ell}(k) \psi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{k}, \hat{z}) \\
&= \sum \tilde{h}^{mn\ell}(k) \phi_{oo}^{mn\ell}(\omega_1, \omega_2, \hat{R}) .
\end{aligned}$$

Therefore  $\tilde{h}^{mn1}(k)$  is equivalent to  $\tilde{h}_{oo}^{mn1}(k)$  in equation (2.47) and equation (F.8) is equivalent to (2.47).

(b) Totally Aligned System

Substituting (F.3) into (F.1) and using the orthogonality condition (C7) in Appendix 2.3, we obtain

$$\mu' = 0 \quad (F.10)$$

Thus

$$\tilde{h}_{oo}^{mn\ell}(k) = \tilde{c}_{oo}^{mn\ell}(k) + \sum_{\substack{n'1' \\ 1''m'}} \rho \tilde{c}_{oo}^{mn'1'}(k) \quad (F.11)$$

$$\tilde{h}_{oo}^{m'n1''}(k) \begin{pmatrix} 1' & 1'' & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 (2\ell + 1)$$

Using the definition

$$\tilde{h}^{\ell}(k) = \sum_{m,n} \tilde{h}_{oo}^{mn\ell}(k) \quad (F.12)$$

we obtain

$$\tilde{h}^{\ell}(k) = \tilde{c}^{\ell}(k) + \sum_{1'1''} \rho \begin{pmatrix} 1' & 1'' & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \tilde{c}^{1'}(k) \tilde{h}^{1''}(k) (2\ell + 1) \quad (\text{F.13})$$

In the limit of  $\underline{\omega}_i = (\alpha_i, \beta_i, \vartheta_i)$  approaching  $(\alpha_i, 0, \vartheta_i)$

$$\psi_{\mu\nu}^{mn\ell}(\underline{\omega}_1, \underline{\omega}_2, \hat{\underline{r}}, \hat{\underline{z}}) \sim \delta_{\mu,0} \delta_{\nu,0} P_{\ell}(\cos\theta)$$

where  $\theta$  is the angle between the z-axis of  $\hat{\underline{r}}$  and the z axis of  $\underline{z}$ .

Therefore

$$\begin{aligned} h(1,2) &= \sum_{\substack{mn\ell \\ \mu\nu}} h_{\mu\nu}^{mn\ell}(r) \psi_{\mu\nu}^{mn\ell}(\underline{\omega}_1, \underline{\omega}_2, \hat{\underline{r}}, \hat{\underline{z}}) \\ &\sim \sum_{mn\ell} h_{00}^{mn\ell}(r) P_{\ell}(\cos\theta) \\ &\sim \sum_{\ell} h^{\ell}(r) P_{\ell}(\cos\theta) \quad . \end{aligned}$$

## CHAPTER 3

## ISOTROPIC SYSTEMS OF DIPOLES

3.1 Introduction

Consider a system of hard or soft spheres imbedded with dipoles. The van der Waals concept of liquids suggests for high densities, the angle-averaged component of the pair correlation function  $g^{000}{}^\dagger(r)$  should resemble the pair correlation function  $g_{HS}$  or  $g_{SS}$  of a hard sphere or soft sphere fluid. Figure 3.1 illustrates the resemblance between  $g_{HS}(r)$  and  $g^{000}(r)$  for a hard sphere dipolar fluid. Numerical schemes, which adequately describe the steric effects, usually have little difficulty in describing  $g^{000}(r)$ .

The main difficulty with dipoles is the description of the orientation of dipolar particles about any particular particle. As mentioned in Chapter 1 the dipoles tend to align with local field. The function ( $g^{112}(r) = h^{112}(r)$ ) describes how closely the particles lie in the field created by any single particle and, because of this, is closely related to the electrostatic energy. Again, for high densities, schemes that deal adequately with the steric effects of the system usually give a good description of  $g^{112}(r)$  and hence the energy.

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† In dipolar fluids the molecular properties are cylindrically symmetric so lower indices are zero, and for this chapter shall be suppressed.

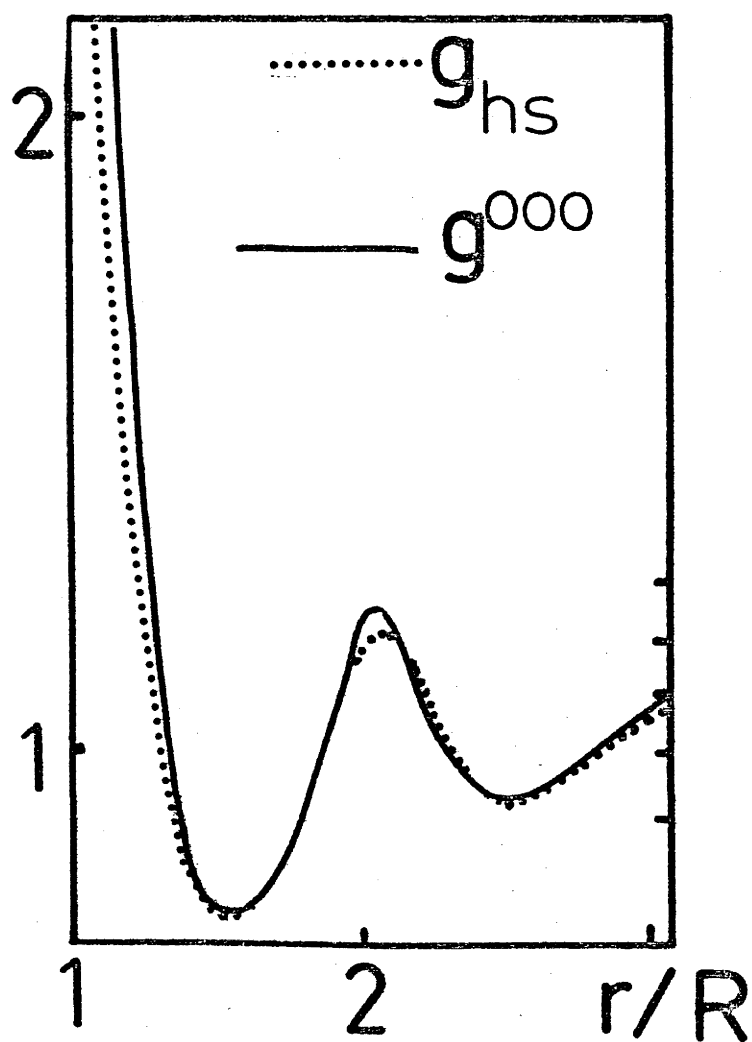


Fig. 3.1 A comparison of the correlation functions of the hard sphere fluid, with that of a dipolar hard sphere fluid.

The calculation of  $(g^{110}(r) = h^{110}(r))$  does cause problems. This measures the average of the cosine between the two dipoles at a separation  $r$ . This function is intrinsically related to the dielectric constant. The structure and long-range nature of  $g^{110}(r)$  seems to be very sensitive to the approximations used; and any changes in  $g^{110}(r)$  strongly affect the dielectric constant.

These three terms,  $g^{000}(r)$ ,  $h^{110}(r)$ ,  $h^{112}(r)$  seem to be important in describing the system. Previous numerical schemes have restricted the  $\phi^{mnl}$ 's to the subset

$$S_3 = \{\phi^{000}, \phi^{110}, \phi^{112}\}$$

so that only these 3 terms are used. However, a recent computer simulation [1] has suggested that the more appropriate subset is

$$S_5 = \{\phi^{000}, \phi^{110}, \phi^{112}, \phi^{220}, \phi^{222}, \phi^{224}, \phi^{022}\}$$

The main problem is not whether these higher terms are needed to describe  $g(1,2)$  accurately but whether they are needed to describe the physical properties accurately. This will be discussed later.

### 3.2 Perturbations, Simulations and Integral Equations

It is not possible to give a detailed survey of the literature on dipolar fluids, but merely an outline of the methodologies of the most successful schemes.



(a) Semi-Macroscopic Approach

A considerable amount of work on polar fluids has been based on an approach used by Bell [2] and Onsager [3]. In this scheme, a point dipole in a spherical cavity is immersed in a continuum of the polar fluid. The dipole exerts a field on the surrounding continuum, which in turn exerts a 'reaction field' on the dipole. It is found that for a permanent (non-polarisable) dipole the reaction field is given by

$$\bar{R} = \frac{1}{3} \left( \frac{2\epsilon - 2}{2\epsilon + 1} \right) \frac{\mu}{a} \quad (3.1)$$

where  $a$  is the radius of the cavity,  $\epsilon$  is the dielectric constant of the bulk fluid and  $\mu$  is the dipole of the particle. If the particle is meant to be identical to the other particles in the fluid, then the choice of  $a$  seems arbitrary. Bell chose  $a$  to be the molecular radius but it seems that Onsager's choice of half the average separation of the particles may be more appropriate. Neither approach is adequate since it is assumed that the surrounding particles resemble a continuum even at separation of one molecular diameter. As will be seen, structure persists at large separations, so the particle nature of the surrounding fluids needs to be used.

(b) Perturbation Schemes

The obvious way to include the effect of individual particles is to consider the dipole-dipole interaction

$$u_{DD}^{(1,2)} = - \frac{\sqrt{30} \mu^2}{r_{12}^3} \Phi^{112}(\omega_1, \omega_2, \hat{R}) \quad (3.2)$$

as a perturbation to the steric effects, the behaviour of which is well known. The 'Pople' expansion is easy to use and quite accurate for high densities and low dipole moments [4-9]. A more robust scheme [10-13] is based on a perturbation about a reference system in which the particles interact via a potential  $\bar{u}$  where

$$e^{-\beta \bar{u}(r_{12})} = \frac{1}{(4\pi^2)} \int d\omega_1 \int d\omega_2 e^{-\beta u_o(r_{12}) - \beta u_{DD}^{(1,2)}} \quad (3.3)$$

For a hard sphere

$$u_o(r_{12}) = \begin{cases} \infty & r_{12} < R \\ 0 & r_{12} > R \end{cases}, \quad (3.4)$$

$R$  being the diameter of the particles. For both schemes convergence can be enhanced by the use of Padé approximants. Nonetheless the very nature of the scheme means that they cannot be used in cases where the dipolar interaction is dominant.

### (c) Computer Simulations

Because of the long-ranged nature of the dipole-dipole potential there has not been the same success in simulating polar fluids as in simulating simple fluids. There are a number of related problems

- (a) The system takes much longer to reach equilibrium.

- (b) For liquids; the maximum size of the central cell that can be simulated is about 3 diameters. Unfortunately, the fluid is still structured at that separation; so that despite the methods using reaction field [14-17] and Ewald summation [18-20], there is a distortion of the correlation functions. Like Onsager, one wants the fluid to resemble a continuum at the edge of the cavity. Indications are that a cavity of a radius of about 10 diameters is needed to achieve this. A recent paper [21] allows fluctuations at the edge of the cell.
- (c) The dielectric constant seems sensitive to the boundary conditions.

(d) Integral Equations

Wertheim [22] made the first major step towards solving the O-Z equation for multipolar fluids when he used the MSA closure to describe dipolar fluids. The MSA solution for quadrupolar fluids described in Chapter 4 is similar to that for dipolar fluids. In many respects the MSA was worse than the perturbation schemes.

A variant of the MSA that needs to be solved numerically is the LHNC (or SSCA) introduced independently by Patey [23] and Wertheim [24]. Instead of linearising the HNC closure to the extent of obtaining the MSA, only the angular components are linearised. This actual method of linearisation will be described in detail later. The other approximation the QHNC [23] will also be described.

### 3.3 A Mathematical Result

At low densities the correlation function  $g(1,2)$  asymptotes as follows

$$g(1,2) \sim e^{-\beta u(1,2)} \quad \text{as} \quad \rho \rightarrow 0. \quad (3.5)$$

Thus

$$h_{(r)}^{mn\ell} \sim \int \Phi^{mn\ell}(\omega_1, \omega_2, \hat{R}) \exp(-\beta U_{DD}) d\omega_1 d\omega_2 - 1 \quad (3.6)$$

where  $U_{DD}$  is given in (3.2). The following (more general) expression is evaluated in Appendix 3.1:

$$B^{mn\ell} = \int \Phi^{mn\ell}(\omega_1, \omega_2, \hat{R}) \exp(f^{000} + f^{110} \Phi + f^{110} \Phi + f^{112} \Phi + f^{112} \Phi) \quad (3.7)$$

and is found to be

$$B^{mn\ell} = \sum_{M=0}^{\infty} \sum_{N=0}^{\infty} a(mn\ell/MN) i_M(f^{110} + f^{112}) i_N(3f^{112}) \exp(f^{000}(r)) \quad (3.8)$$

where  $i_n(z)$  is a modified spherical Bessel function of the first kind [25]. The coefficient  $a(mn\ell/MN)$  is given by

$$a(mn\ell/MN) = (-1)^{N+m+\ell} (2N+1) (2M+1) (2m+1) (2n+1) (2\ell+1) \begin{pmatrix} M & N & m \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} M & N & n \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} N & m & M \\ n & N & \ell \end{matrix} \right\} \sum_{q=-N}^N \begin{pmatrix} N & N & \ell \\ q & -q & 0 \end{pmatrix}. \quad (3.9)$$

Selected values of  $a(mn\ell/MN)$  that are useful in our discussion is

given in Appendix 3.2.

### 3.4 The Percus Yevick Closure

The PY closure is given by

$$c(1,2) = F(1,2) (1 + h(1,2)) \quad (3.10)$$

where  $\beta = 1/kT$ ,  $\eta \equiv h - c$  and

$$\begin{aligned} F(1,2) &= \exp(-\beta u(1,2)) - 1 \\ &\equiv \sum_{mnl} F^{mnl}(r_{12}) \phi^{mnl}(\omega_1, \omega_2, \hat{r}_{12}). \end{aligned} \quad (3.11)$$

$F^{mnl}(r_{12})$  can be calculated using the equation in the previous section.

In principle, the PY closure can be calculated to arbitrary accuracy. However there is a limited amount of computing time so that only a finite number of rotational invariants can be considered.

If the subset of rotational invariants is restricted to the spherically symmetric component, i.e.  $(mnl) = (000)$  the PY closure becomes

$$c^{000}(r_{12}) = F^{000}(r_{12}) (1 + \eta^{000}(r_{12})) \quad (3.12)$$

$$= [\exp(-\beta u(r_{12})) - 1] (1 + \eta^{000}(r_{12})) \quad (3.13)$$

where  $\bar{u}$  has been defined in equation (3.3).

In other words keeping only the spherically symmetric component is equivalent to solving the PY equation for a simple fluid with the angle averaged dipole-dipole potential. In contrast, the spherically symmetric component of the correlation functions in the MSA or LHNC approximation does not contain any information about the dipolar nature of the fluid molecules. It is interesting to note that Monte Carlo pair distribution functions calculated using  $\bar{u}$  compares very favourably with the exact angle averaged pair distribution functions. Also because  $\bar{u}$  already contains information about the dipolar part of the pair potential, it is a more accurate reference potential for perturbation theories [10].

Since the PY closure (3.10) is a linear relationship between  $c$  and  $\eta$  it is easy to vary the size of the subset of rotational invariants we wish to retain. To demonstrate this, we need one additional result (Appendix 3.3)

$$\begin{aligned} \Phi^{mnl}(\omega_1, \omega_2, \omega_3) \Phi^{m'n'l'}(\omega_1, \omega_2, \omega_3) \\ = \sum_{MNL} b(MNL) \Phi^{MNL}(\omega_1, \omega_2, \omega_3) \end{aligned} \quad (3.14)$$

where the coefficient  $b(MNL)$  is

$$\begin{aligned} b(MNL) = (2M + 1) (2N + 1) (2L + 1) \begin{pmatrix} m & m' & M \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n & n' & N \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} m & m' & M \\ n & n' & N \\ l & l' & L \end{Bmatrix} \end{aligned} \quad (3.15)$$

in which  $\begin{Bmatrix} m & m' & M \\ n & n' & N \\ l & l' & L \end{Bmatrix}$  is a Wigner 9-j symbol [32].

The coupling matrix which relates the various components of  $c$  and  $\eta$  can now be evaluated with the aid of (3.7)-(3.11), (3.14) and (3.15). If we choose to represent  $c$  and  $\eta$  in terms of the subset  $S_3$ , the PY closure condition will have the form

$$\begin{pmatrix} c^{000} \\ c^{110} \\ c^{112} \\ c \end{pmatrix} = \begin{pmatrix} F^{000} & F^{110/9} & F^{112/45} \\ F^{110} & F^{11} & F^{12} \\ F^{112} & G^{21} & G^{22} \\ F & G & G \end{pmatrix} \begin{pmatrix} 1 + \eta^{000} \\ \eta^{110} \\ \eta^{112} \\ \eta \end{pmatrix} \quad (3.16)$$

$$G^{11} = F^{000} + 2 \times 5^{-3/2} F^{220} \quad (3.17)$$

$$G^{12} = (7^{1/2}/5^3) F^{222} - (2^{1/2}/5^2) F^{202} \quad (3.18)$$

$$G^{21} = G^{12}/5 \quad (3.19)$$

$$\begin{aligned} G^{22} = & F^{000} + 5^{-5/2} F^{220} + (2/5^5 \times 7)^{1/2} F^{222} \\ & + 3(2^3/5^5 \times 7)^{1/2} F^{224} + (22 \times 3^{1/2}/35) F^{022} \end{aligned} \quad (3.20)$$

when a subset larger than  $S_3$  is required to represent  $c$  and  $\eta$ , a new coupling matrix analogous to that in (3.16) can be computed in a similar manner. The new subset must, of course be closed under the OZ angular convolution.

The PY closure gives the correct low density form

$$h(1,2) \rightarrow \exp(-\beta u(1,2)) - 1$$

even when truncated as described. Furthermore it will contain the

correct contribution from the second dielectric virial coefficient.

### 3.5 The Hypernetted Chain Approximation

The HNC closure is given by

$$1 + h(1,2) = \exp[-\beta u(1,2) + h(1,2) - c(1,2)] \quad (3.21)$$

and the truncation scheme for this equation is as follows. If we choose to represent  $c$  and  $h$  in terms of a finite subset of rotational invariants,  $S$  say, we shall only retain the coefficients belonging to the same subset in an invariant expansion of the right hand side of (3.21). Using the shorthand  $\eta = h - c$  we write the right hand side of (3.21) as

$$E(1,2) \equiv \exp[-\beta u(1,2) + \sum_S \eta^{mnl}(r_{12}) \phi^{mnl}(\underline{\omega}_1, \underline{\omega}_2, \hat{R})] \quad (3.22)$$

$$\approx \sum_S E^{mnl}(r_{12}) \phi^{mnl}(\underline{\omega}_1, \underline{\omega}_2, \hat{R}) . \quad (3.23)$$

The subscript  $S$  under the summation sign denotes a sum over only the subset  $S$  of chosen rotational invariants. In general, an infinite number of terms is needed to represent even a finite sum in the exponential function in (3.22), but our truncation scheme only retains those invariants in (3.23), that are members of the originally chosen subset. Clearly, the rotational invariants contained in the subset  $S$  must form a closed set under the OZ angular convolution. If we only keep the spherically symmetric components of



c and h the truncated HNC closure becomes

$$1 + h^{000}(r_{12}) = \exp[-\beta \bar{u}(r_{12}) + h^{000}(r_{12}) - c^{000}(r_{12})] \quad (3.24)$$

where  $\bar{u}$  is the angle averaged potential. Analogous to the similar PY result, this scheme corresponds to the HNC approximation for a simple fluid interacting with the angle averaged potential,  $\bar{u}$ .

The next obvious subset to consider is  $S_3$ . In this case the HNC closure is

$$1 + h^{000} + h^{110} \phi^{110} + h^{112} \phi^{112} = \exp[(\eta^{000} - \beta u^{000}) + \eta^{110} \phi^{110} + (\eta^{112} - \beta u^{112}) \phi^{112}] \quad (3.25)$$

$$\approx E_3^{000}(r_{12}) + E_3^{110}(r_{12}) \phi^{110} + E_3^{112}(r_{12}) \phi^{112}. \quad (3.26)$$

Thus the truncated HNC closure becomes

$$\begin{aligned} 1 + h^{000}(r_{12}) &= E_3^{000}(r_{12}), \\ h^{110}(r_{12}) &= E_3^{110}(r_{12}), \\ h^{112}(r_{12}) &= E_3^{112}(r_{12}), \end{aligned} \quad (3.27)$$

where the functions  $E_3^{000}$ ,  $E_3^{110}$ ,  $E_3^{112}$  may be obtained using (3.7)-(3.9). This truncation scheme provides a non-linear coupling between the three angular components of the correlation function and it is easy to see that in the low density limit ( $\eta \rightarrow 0$ ) the various

components  $h^{mn1}$  will have the correct asymptotic behaviour.

The LHNC approximation is equivalent to linearizing the HNC closure with respect to the (110) and (112) components, that is,

$$1 + h^{000} + h^{110} \Phi^{110} + h^{112} \Phi^{112} \approx \exp[\eta^{000} - \beta u^{000}] \quad (3.28)$$

$$\left\{ 1 + \eta^{110} \Phi^{110} + (\eta^{112} - \beta u^{112}) \Phi^{112} \right\} .$$

Thus by equating coefficients in (3.28) we get

$$\begin{aligned} 1 + h^{000} &= \exp(\eta^{000} - \beta u^{000}) , \\ h^{110} &= (1 + h^{000}) \eta^{110} , \\ h^{112} &= (1 + h^{110}) (\eta^{112} - \beta u^{112}) , \end{aligned} \quad (3.29)$$

which defines the LHNC approximation. The result in (3.29) can also be obtained from a linearization of (3.27) with respect to the (110) and (112) components which can be easily verified by using (3.7) (3.9), and the known small argument expressions of the modified Bessel functions,  $i_n(x)$  [25].

The QHNC approximation is derived in a slightly different manner [23]. Equation (3.25) is rewritten as

$$\ln(1 + h^{000} + h^{110} \Phi^{110} + h^{112} \Phi^{112}) = (\eta^{000} - \beta u^{000}) \quad (3.30)$$

$$+ \eta^{110} \Phi^{110} + (\eta^{112} - \beta u^{112}) \Phi^{112} .$$

The left hand side is then expanded to quadratic order in the (110) and (112) components, but only those quadratic terms that contribute to the (000) component are retained. In the present notation, the QHNC approximation reads

$$\begin{aligned}
 1 + h^{000} + h^{110} \phi^{110} + h^{112} \phi^{112} &= \exp[(\eta^{000} - \beta u^{000}) \\
 + (\eta^{110})^2/18 + (\eta^{112} - \beta u^{112})^2/90] &(1 + \eta^{110} \phi^{110} \\
 + (\eta^{112} - \beta u^{112}) \phi^{112}) &. \quad (3.31)
 \end{aligned}$$

It is now clear that by truncating the HNC closure in such a way as to include all non-linear contributions to the subset  $S_3$  we can recover the expected low density behaviour of the correlation functions, and in particular include the correct contribution from the second dielectric virial coefficient to the dielectric constant. The obvious price is the more complicated coupling conditions between the various angular components.

### 3.6 The work of Gaylor, Isbister, Watts

Recently, another numeric scheme has emerged, which has the correct low density limit, yet approaches the LHNC at high densities. Gaylor et al [26] have developed the scheme for soft spheres. In terms of  $y(1,2)$  where

$$y(1,2) \equiv \exp(\beta u(1,2)) (1 + h(1,2)) \quad (3.32)$$

the HNC can be written

$$c(1,2) = (1 + F(1,2)) y(1,2) - 1 - \log(y(1,2)) \quad (3.33)$$

where  $F(1,2)$  is defined in (3.11). Linearising the final term in the manner of Patey [23] and equating coefficients yields the final equations

$$\begin{aligned} c^{000} &= (1 + F^{000}) y^{000} - 1 - \log y^{000} + \frac{1}{9} F^{110} y^{110} \\ &+ \frac{F^{112} y^{112}}{45} \end{aligned} \quad (3.34)$$

$$c^{110} = F^{110} y^{000} + y^{110} \left[ F^{000} - \frac{1}{y^{000}} \right] \quad (3.35)$$

$$c^{112} = F^{112} y^{000} + y^{112} \left[ F^{000} - \frac{1}{y^{000}} \right] . \quad (3.36)$$

Apart from the log term in (3.34) this <sup>is</sup> a truncated form of the PY closure.

### 3.7 Lado's scheme

An important facet of the LHNC and the QHNC closures is the use of a numeric scheme developed by Lado [27]. As already stated, it is important to model steric effects properly and yet it is well known that the HNC does not realistically model repulsive potentials. To

overcome this, the correlation functions  $f(= h, c)$  are separated into 2 components

$$f(1,2) = f_{HS}(1,2) + \Delta f(1,2). \quad (3.37)$$

The HNC would then take the form

$$\Delta h = h_{hs} (\exp(\Delta h - \Delta c - \beta U_{DD}) - 1). \quad (3.38)$$

Instead of using the HNC expression for  $h_{hs}$ , a better approximation is used. Both Patey and ourselves use the Verlet-Weis [28] approximation, although a computer simulation can also be used. This method is not only applicable to hard spheres but to soft spheres and bodies of general shape.

### 3.8 Results: Truncated HNC closure

We give some numerical results for a hard sphere dipolar fluid, calculated using the truncated HNC (THNC) closure as defined by (3.25) - (3.27). The numerical method is similar to that of Patey [23] in which the OZ equation was solved by iteration using the Fast Fourier Transform method. The set of equations (2.43-49) are solved together with the THNC closure.

#### (i) Correlation functions

In figures 3.2 and 3.3 the THNC  $g^{000}$  are shown. The difference between this and that obtained by the QHNC is comparable with

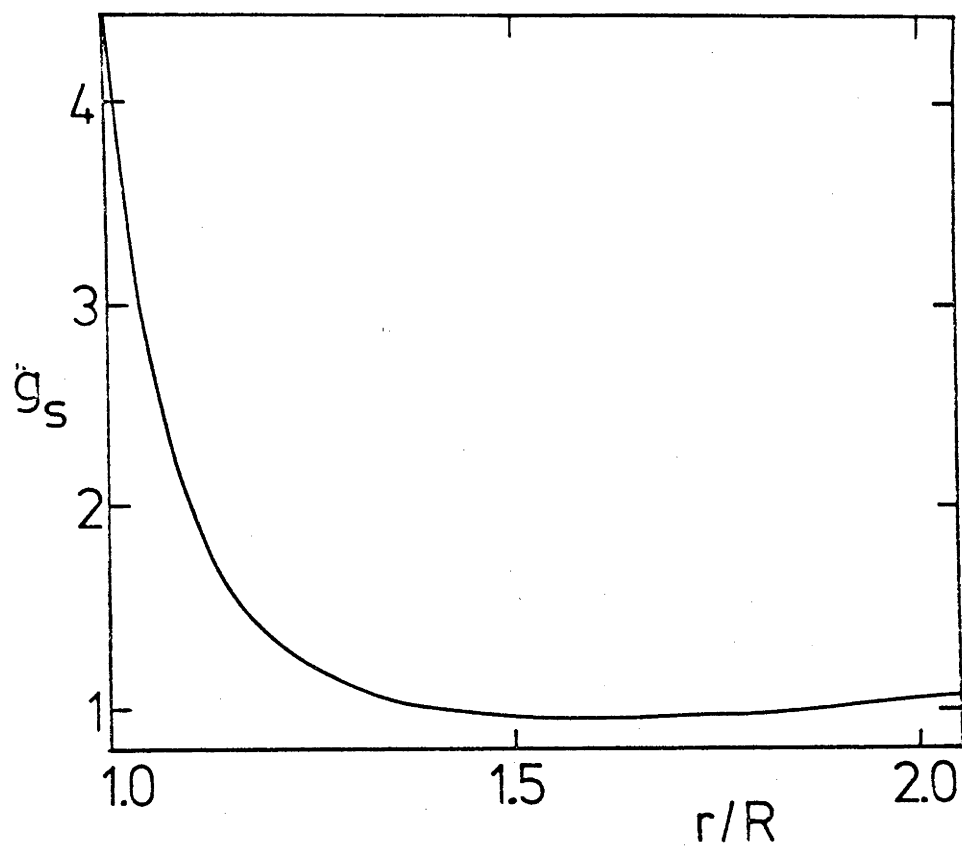


Fig. 3.2 The component  $g_s (=g^{000})$  of the pair correlation function at  $\rho^* = 0.2$ ,  $\mu^{*2} = 2.75$

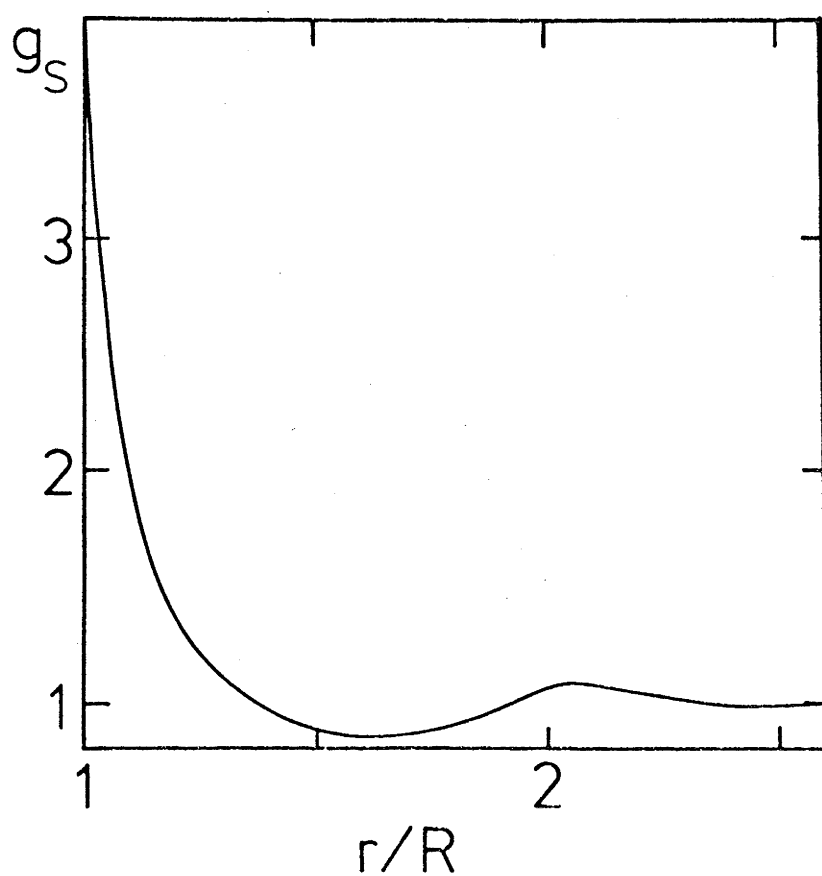


Fig. 3.3 As in Fig. 3.2 but  $\rho^* = 0.6$

numerical uncertainties. From figure 3.5 we see that the THNC solution for  $h^\Delta \equiv -3^{1/2} h^{110}$  is consistently higher than the QHNC values. This means that the THNC would predict a higher value for the dielectric constant.

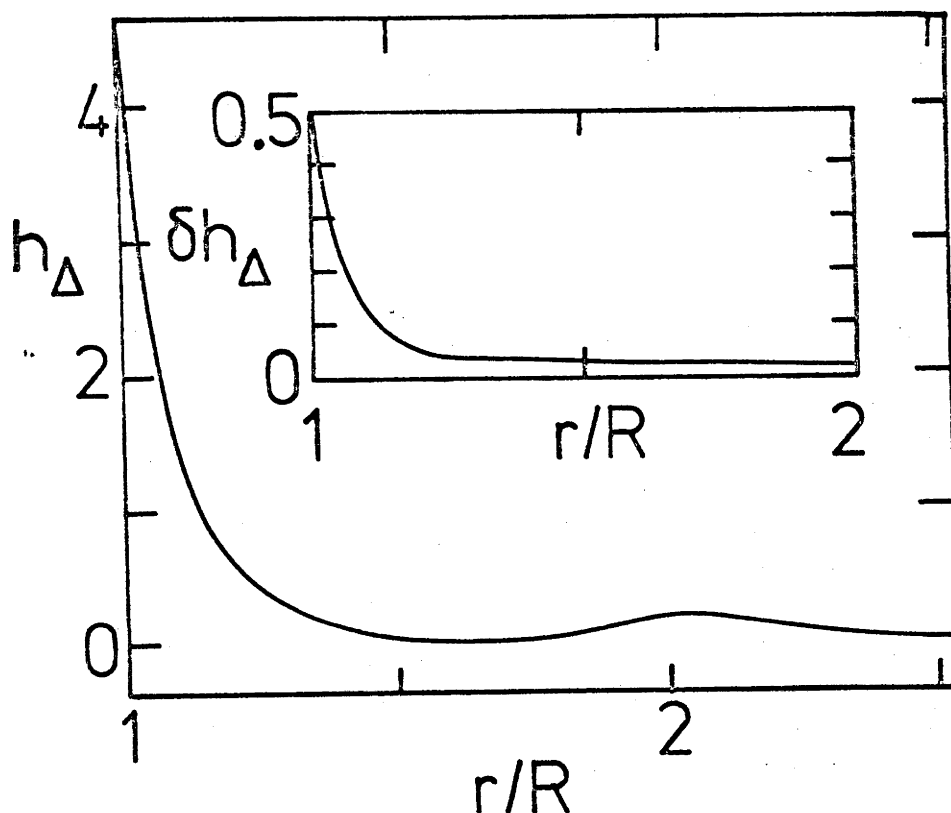


Fig. 3.4 The component  $h^\Delta (= -h^{110}/3^{1/2})$  of the pair correlation function  $\rho^* = 0.6$ ,  $\mu^{*2} = 2.75$

The component  $h^D \equiv (30)^{1/2} h^{112}$  is given in figures 3.5 and 3.6. The difference between the THNC and QHNC occurs close to contact and becomes negligible at high densities.

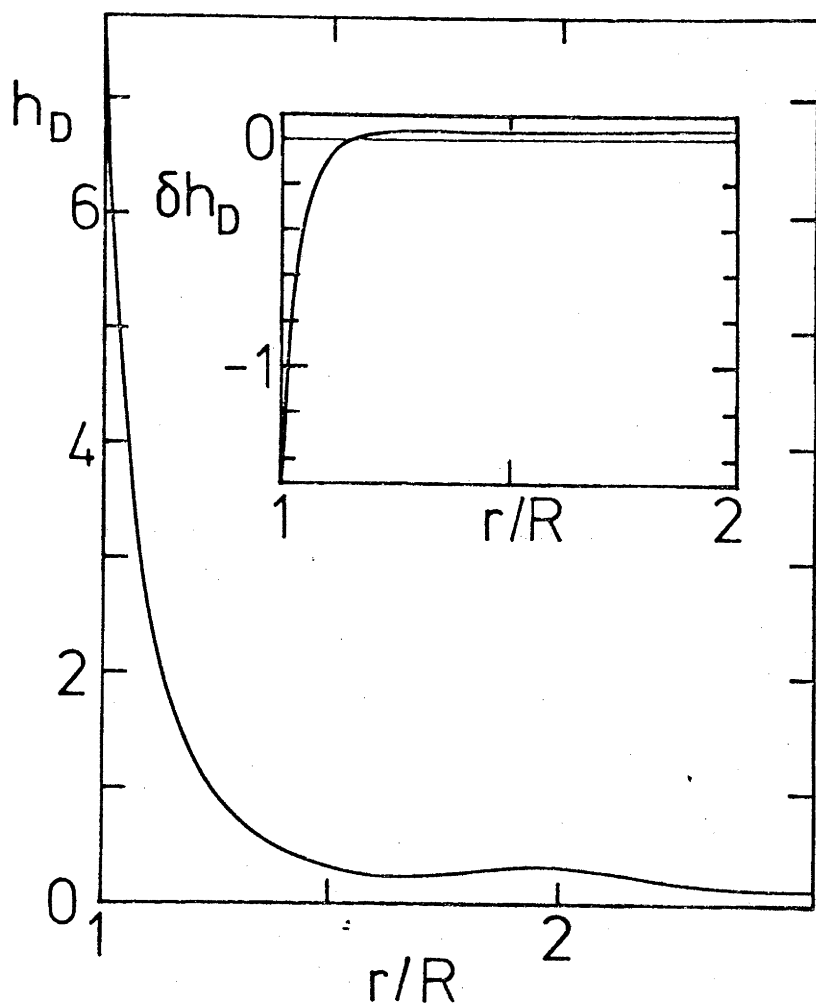
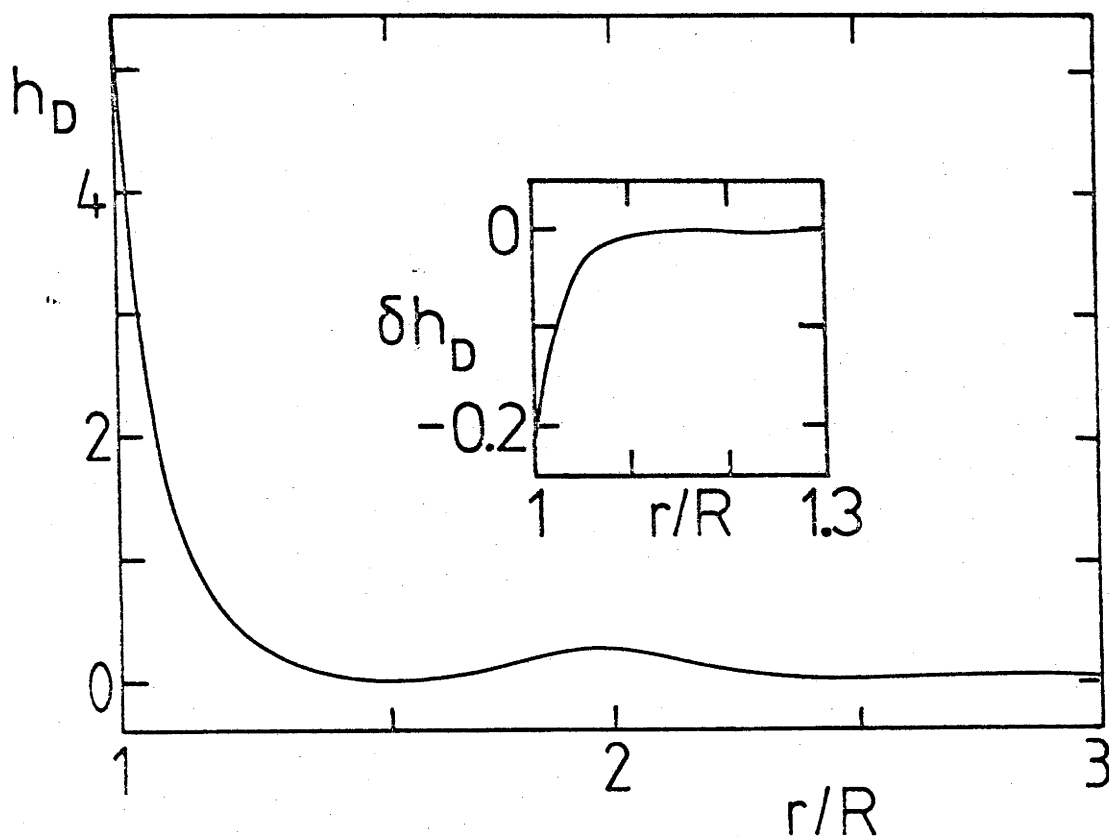


Fig. 3.5 The component  $h_D = (h^{112}/(30)^{1/2})$  of the pair correlation function at  $\rho^* = 0.2$ ,  $\mu^* = 2.75$

Fig. 3.6 As for Fig. 3.5 but  $\rho^* = 0.6$ .





(ii) Energy

The internal energy,  $U$  is given by

$$U/NkT = -(4\pi\rho\mu^2/3kT) \int_R^\infty dr r^{-1} h^{112}(r) , \quad (3.39a)$$

$$= (4\pi\rho\mu^2/9kT) \hat{h}^{112}(r), \quad r < R , \quad (3.39b)$$

$$= (4\pi\rho\mu^2/9kT)(\hat{\eta}^{112}(r) + \hat{c}^{112}(r)), \quad r < R , \quad (3.39c)$$

where ( $f = h, c$  or  $\eta$ )

$$\hat{f}^{112}(r) = f^{112}(r) - 3 \int_r^\infty dr' r'^{-1} f^{112}(r') . \quad (3.40)$$

Equation (3.39c) was used to evaluate  $U$  since the right-hand side is a quantity which occurs naturally in the iterative solution of the OZ equation. The results are given in table 3.1. There is almost no difference between the THNC and QHNC closures.

(iii) Dielectric constant

The dielectric constant,  $\epsilon$  is calculated from the Kirkwood formula

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = yg , \quad (3.41)$$

where

$$y = 4\pi\rho\mu^2/9kT = 4\pi\rho^* \mu^{*2}/9 . \quad (3.42)$$

Table 3.1 The internal energy ( $-U/NkT$ ) of a hard sphere dipolar fluid for various reduced densities,  $\rho^*$  and dipole moments,  $\mu^*$ .

	$\rho^*$			
$\mu^*$	0.2	0.4	0.6	
1.0	0.290	0.540	0.778	QHNC
	0.286	0.542	0.777	THNC
2.0	1.14	1.78	2.27	QHNC
	1.12	1.77	2.28	THNC
2.75	2.16	2.99	3.62	QHNC
	2.13	3.00	3.64	THNC

and the Kirkwood  $g$ -factor is

$$g = 1 + (4\pi\rho/3) \int_R^\infty dr r^2 h^{110}(r), \quad (3.43a)$$

$$= 1 + (\rho/3) \tilde{h}^{110}(0), \quad (3.43b)$$

$$= 1 + (\rho/3) \sum_{x=-1}^1 \begin{pmatrix} 1 & 1 & 0 \\ x & -x & 0 \end{pmatrix} \tilde{h}_x^{11}(0), \quad (3.43c)$$

$$= 1 + (\rho/3) \sum_{x=-1}^1 \begin{pmatrix} 1 & 1 & 0 \\ x & x & 0 \end{pmatrix} \frac{\tilde{c}_x^{11}(0)}{1 - (\rho/3) \tilde{c}_x^{11}(0)}. \quad (3.43d)$$

The quantities in (3.43d) occur naturally in the iterative solution

and when tested on the MSA, it was found to be more accurate than evaluating the integral in (3.43a).

Values of the dielectric constant are given in table 3.2. The larger values of  $\epsilon$  predicted by the THNC reflects the larger magnitude of the  $h^{110}(r)$  components of the total correlation function.

Table 3.2      The dielectric constant,  $\epsilon$  of a hard sphere dipolar fluid for various reduced densities,  $\rho^*$  and dipole moments,  $\mu^*$ .

$\rho^*$				
$\mu^*$	0.2	0.4	0.6	
1.0	2.07	3.63	5.84	QHNC
	2.09	3.71	6.03	THNC
2.0	3.62	8.28	16.9	QHNC
	3.93	9.39	19.2	THNC
2.75	5.16	13.5	32.4	QHNC
	6.28	16.9	39.3	THNC

### 3.9 Discussion

We have proposed a method for studying the PY and HNC approximations for dipolar fluids using a truncated set of rotational invariants to represent the pair correlation functions. For a given subset of rotational invariants, this method includes all non-linear

effects that arise from the closure condition. As a result, all the correlation functions become exact in the low density limit, and, in particular, the contributions to the dielectric constant from the second dielectric virial coefficient are included. By a suitable linearization procedure our method reduces to the LHNC approximation. For the PY approximation, it is also particularly easy to vary the size of the subset of rotational invariants to consider effects due to subset size.

Preliminary numerical results given here using the THNC based on the subset  $S_3$  suggest that in the range of densities and dipole moments considered, properties such as the internal energy,  $g^{000}$  and  $h^{112}$  are not particularly sensitive to the non-linear terms, as one would expect. There is little difference between the QHNC and THNC values for these quantities. However, the non-linear contributions do appear to make a difference for the dielectric constant,  $\epsilon$  and  $h^{110}$ . This last observation thus raises the possibility that rotational invariants outside the subset  $S_3$  may also affect  $\epsilon$  and  $h^{110}$ . The next set of low index invariants which is closed with the OZ angular convolution is

$$S_7 = \{1, \Phi^{110}, \Phi^{112}, \Phi^{202}, \Phi^{220}, \Phi^{222}, \Phi^{224}\} . \quad (3.44)$$

Patey et al, [29] had used a similar subset by omitting the (202) projection to study a dipolar fluid. The (202) term was not included

because they originally considered a hard sphere-dipole-linear quadrupole fluid and took the subset of rotational invariants that arises in the Mean Spherical Approximation (MSA). It is difficult to establish a priori why the (202) term (which arises from the product  $\phi^{110} \phi^{112}$ ) needed to be included, although its inclusion may explain why the results for a pure dipolar fluid seem to deteriorate when the MSA dipole-linear quadrupole subset is used.

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### Appendix 3.1 Expansion of the Boltzmann Factor and Related Formulae.

We give details of the expansion formula for the Boltzmann factor

$$B = \exp[-3^{1/2} f^{110}(r) \phi^{110}(\omega_1, \omega_2, \hat{r}) + (120)^{1/2} f^{112}(r) \phi^{112}(\omega_1, \omega_2, \hat{r})] \quad (\text{A.1})$$

$$= \sum_{mnl} B^{mnl}(r) \phi^{mnl}(\omega_1, \omega_2, \hat{r}) \quad (\text{A.2})$$

The coefficients  $B^{mnl}$  are calculated using a technique that is a generalization of that used by White [30]. Two steps are involved.

The first is to rewrite  $B$  as

$$B = \exp[f^{110}(r) \cos \theta_2 + f^{112}(r) (\cos \theta_2 + 3 \cos \alpha)] \quad (\text{A.3})$$

where  $\theta_2$  and  $\alpha$  will be defined later. The second step is to use the identity [8]

$$\exp(z \cos \theta) = \sum_{n=0}^{\infty} (2n+1) i_n(z) P_n(\cos \theta) \quad (\text{A.4})$$

where  $i_n(z)$  is a modified spherical Bessel function and  $P_n(\cos \theta)$  a Legendre Polynomial. This will produce a linear combination of terms of the form  $P_n(\cos \theta_2) P_n(\cos \alpha)$  which can then be manipulated to the required form in (A2). The details are as follows.

A co-ordinate system is chosen so that the  $z$ -axis is in the direction of  $\bar{\mu}_1(\omega_1)$  so that  $\bar{\mu}_2(\omega_2)$  and  $\hat{r}$  are given by

$$\bar{\mu}_2 = (\theta_2, \phi_2) \quad (\text{A.5})$$

$$\hat{r} = (\theta, \phi) \quad (\text{A.6})$$

where  $\theta, \phi$  are the polar and azimuthal angles respectively. The following relations can then be obtained

$$\Phi^{110} \equiv -3^{1/2} \hat{\mu}_1 \cdot \hat{\mu}_2 = -3^{1/2} \cos \theta_2 \quad (\text{A.7})$$

$$\Phi^{112} \equiv -(30)^{1/2} [(\hat{\mu}_1 \cdot \hat{\mu}_2) - 3(\hat{\mu}_1 \cdot \hat{r})(\hat{\mu}_2 \cdot \hat{r})] \quad (\text{A.8})$$

$$= (120)^{1/2} (\cos \theta_2 + 3 \cos \alpha)$$

where

$$\cos \alpha \equiv \cos \theta_2 \cos 2\theta + \sin \theta_2 \sin 2\theta \cos \phi_2 \quad (\text{A.9})$$

and hence (A.3) follows.

Now using (A.4), we can write (A.3) as

$$B = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (2n+1)(2m+1) i_n (3f^{112}) i_m (f^{110} + f^{112}) P_m(\cos \theta_2) P_n(\cos \alpha). \quad (\text{A.10})$$

From (A.9) and the addition theorem for Legendre Polynomials [31] we have

$$\begin{aligned}
 P_n(\cos \alpha) &= \sum_{v=-n}^n \frac{(n-|v|)!}{(n+|v|)!} P_n^v(\cos \theta_2) P_n^v(\cos \theta_2) e^{iv\phi_2} \\
 &= \sum_{v=-n}^n (-1)^{v-|v|} D_{ov}^n(0, 2\theta, 0) D_{ov}^n(\phi_2, \theta_2, 0) \quad .
 \end{aligned}
 \tag{A.11}$$

Using the identities (Appendix 2.1)

$$D_{ov}^n(0, 2\theta, 0) = \sum_{\mu=-n}^n D_{o\mu}^n(0, \theta, 0) D_{\mu v}^n(0, \theta, 0) \tag{A.12}$$

$$D_{o\mu}^n(0, \theta, 0) = D_{-\mu o}^n(0, \theta, 0) \tag{A.13}$$

and the product formula (Appendix 2.1)

$$\begin{aligned}
 D_{\lambda o}^n(0, \theta, 0) D_{\mu v}^n(0, \theta, 0) &= \sum_{l=0}^{2n} \sum_{\mu', v'} (2l+1) \begin{pmatrix} n & n & l \\ \lambda & \mu & \mu' \end{pmatrix} \\
 &\times \begin{pmatrix} n & n & l \\ 0 & v & v' \end{pmatrix} D_{\mu' v'}^n(0, \theta, 0)
 \end{aligned}
 \tag{A.14}$$

we obtain

$$D_{ov}^n(0, 2\theta, 0) = \sum_{l=0}^{2n} \sum_{\mu=-n}^n (2l+1) \begin{pmatrix} n & n & l \\ -\mu & \mu & 0 \end{pmatrix} \begin{pmatrix} n & n & l \\ 0 & v & -v \end{pmatrix} D_{ov}^l(0, \theta, 0) \tag{A.15}$$

after invoking some standard properties of the 3-j symbols. From (A.12) we can readily obtain the result for the product of the two Legendre polynomials in (A.10)

$$\begin{aligned}
 P_n(\cos\alpha)P_m(\cos\theta_2) &= \sum_{\ell=0}^{2n} \sum_{\mu, \nu=-n}^n (2\ell+1) \begin{pmatrix} n & n & \ell \\ -\mu & \mu & 0 \end{pmatrix} \begin{pmatrix} n & n & \ell \\ 0 & \nu & -\nu \end{pmatrix} \\
 &\times D_{ov}^{\ell}(0, \theta, 0) D_{ov}^n(\phi_2, \theta_2, 0) P_m(\cos\theta_2) \quad .
 \end{aligned}
 \tag{A.16}$$

To complete the derivation, we require two further results (Appendix 2.1)

$$\begin{aligned}
 D_{ov}^n(\phi_2, \theta_2, 0) P_m(\cos\theta_2) &= D_{ov}^n(\phi_2, \theta_2, 0) D_{oo}^m(0, \theta_2, 0) \\
 &= \sum_q (2q+1) \begin{pmatrix} n & m & q \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n & m & q \\ \nu & 0 & -\nu \end{pmatrix} D_{o-\nu}^q(\phi_2, \theta_2, 0)
 \end{aligned}
 \tag{A.17}$$

$$\begin{aligned}
 \begin{pmatrix} n & n & n' \\ 0 & p & -p \end{pmatrix} \begin{pmatrix} m' & n & m \\ p & -p & 0 \end{pmatrix} &= (-1)^{p+m'+n+n'} \sum_r (2r+1) \\
 &\times \begin{pmatrix} m' & r & n' \\ -p & 0 & p \end{pmatrix} \begin{pmatrix} n & r & m \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} n & r & m \\ m' & n & n' \end{matrix} \right\}
 \end{aligned}
 \tag{A.18}$$

to give the final result

$$\begin{aligned}
 B &= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{\ell=0}^{2n} \sum_q \sum_{\mu=-n}^n \sum_{\nu=-n}^n \sum_r (-1)^{n+\ell+q} (2m+1)(2n+1) \\
 &\times (2q+1)(2\ell+1)(2r+1) i_m(f^{110} + f^{112}) i_n(3f^{112}) \begin{pmatrix} m & n & q \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n & n & \ell \\ -\mu & \mu & 0 \end{pmatrix} \\
 &\times \begin{pmatrix} n & r & m \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} n & r & m \\ q & n & \ell \end{matrix} \right\} \Phi^{rq\ell}(\hat{\mu}_1, \hat{\mu}_2, \hat{r}) \quad .
 \end{aligned}
 \tag{A.19}$$

Next we outline the derivation of (3.15). By choosing a coordinate system in which the z-axis is parallel to the vector  $\omega_3$  we can write the product of two rotational invariants as [9]

$$\begin{aligned}
 & \Phi^{mn\ell}(\omega_1, \omega_2, \omega_3) \Phi^{m'n'l'}(\omega_1, \omega_2, \omega_3) \\
 &= \sum_{s,t} \begin{pmatrix} m & n & \ell \\ -s & s & 0 \end{pmatrix} \begin{pmatrix} m' & n' & l' \\ -t & t & 0 \end{pmatrix} D_{o-s}^m(\omega_1) D_{o-t}^{m'}(\omega_1) D_{os}^n(\omega_2) D_{ot}^{n'}(\omega_2) \\
 &= \sum_{s,t} \sum_{m'',n'',u} (2m''+1)(2n''+1) \begin{pmatrix} n & m & \ell \\ -s & s & 0 \end{pmatrix} \begin{pmatrix} m & m' & m'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n & n' & n'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} m' & n' & l' \\ -t & t & 0 \end{pmatrix} \\
 &\times \begin{pmatrix} m & m' & m'' \\ -s & -t & -u \end{pmatrix} \begin{pmatrix} n & n' & n'' \\ s & t & u \end{pmatrix} D_{ou}^{m''}(\omega_1) D_{o-u}^{n''}(\omega_2) \quad . \quad (A.20)
 \end{aligned}$$

But with the aid of the identity [32]

$$\begin{aligned}
 & \sum_{s,t} \begin{pmatrix} \ell & m & n \\ 0 & s & -s \end{pmatrix} \begin{pmatrix} l' & m' & n' \\ 0 & t & -t \end{pmatrix} \begin{pmatrix} m & m' & m'' \\ s & t & u \end{pmatrix} \begin{pmatrix} n & n' & n'' \\ -s & -t & -u \end{pmatrix} \\
 &= \sum_{l''} (2\ell''+1) \begin{pmatrix} \ell & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'' & m'' & n'' \\ 0 & u & -u \end{pmatrix} \left\{ \begin{matrix} m & m' & m'' \\ n & n' & n'' \\ \ell & l' & l'' \end{matrix} \right\} \quad (A.21)
 \end{aligned}$$

(A.20) can be written as

$$\begin{aligned}
 & \Phi^{mn\ell}(\omega_1, \omega_2, \omega_3) \Phi^{m'n'l'}(\omega_1, \omega_2, \omega_3) = \sum_{l''m''n''} \sum_{stu} (2l''+1)(2m''+1)(2n''+1) \\
 &\times \begin{pmatrix} m & m' & m'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n & n' & n'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'' & m'' & n'' \\ 0 & u & -u \end{pmatrix} \left\{ \begin{matrix} m & m' & m'' \\ n & n' & n'' \\ \ell & l' & l'' \end{matrix} \right\} \\
 &\times D_{ou}^{m''}(\omega_1) D_{o-u}^{n''}(\omega_2) \\
 &= \sum_{l''m''n''} (2l''+1)(2m''+1)(2n''+1) \begin{pmatrix} m & m' & m'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n & n' & n'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & l' & l'' \\ 0 & 0 & 0 \end{pmatrix}
 \end{aligned}$$

$$\times \begin{Bmatrix} m & m' & m'' \\ n & n' & n'' \\ \ell & 1' & 1'' \end{Bmatrix} \phi^{m''n''1''}(\omega_1, \omega_2, \omega_3) . \quad (\text{A.22})$$

### Appendix 3.2 Expressions for the coefficient $a(\text{MNL}/mn)$ in (3.8)

We give explicit expressions for some of the coefficients  $a(\text{MNL}/mn)$  (see equation (2.6)) which are useful in deriving results given in the text.

The following results for the 3-j symbols are needed:-

$$\sum_q \begin{pmatrix} n & n & \ell \\ q & -q & 0 \end{pmatrix} = \begin{cases} 0 & , \quad \ell \text{ odd} \\ 2^\ell \frac{(n + \frac{\ell}{2})!}{(n - \frac{\ell}{2})!} \frac{(2n - \ell)!}{(2n + \ell + 1)!}^{1/2} & , \quad \ell = 0, 2, 4, 6 \end{cases} \quad (\text{B.1})$$

$$\begin{pmatrix} n+2 & n & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{3(n+2)(n+1)}{2(2n+5)(2n+3)(2n+1)} \quad (\text{B.2})$$

$$\begin{pmatrix} n & n & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{(n+1)n}{(2n+3)(2n+1)(2n-1)} \quad (\text{B.3})$$

$$\begin{pmatrix} n-2 & n & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{3n(n-1)}{2(2n+1)(2n-1)(2n-3)} . \quad (\text{B.4})$$

The required expressions for the 6-j symbols are given in [33].

The expressions for the coefficients  $a(\text{MNL}/mn)$  are:

$$a(000|mn) = (-1)^n \delta_{m,n} \quad (\text{B.5})$$

$$a(110|mn) = \frac{(-1)^{n+1} 3^{3/2} (m+n+1)}{2(2n+1)} (\delta_{m,n-1} + \delta_{m,n+1}) \quad (\text{B.6})$$

$$a(112|mn) = \frac{(-1)^{n+1} 2^{1/2} 3^{3/2} 5^{1/2} n(n+1)}{(2n+1)(2m+1)} (\delta_{m,n-1} + \delta_{m,n+1}) \quad (\text{B.7})$$

$$a(220|mn) = \frac{(-1)^n 3 \cdot 5^{3/2} (2m+1)(m+n)(m+n+2)}{2^3 (m+n+3)(m+n+1)(m+n-1)} \quad (\text{B.8})$$

$$\times (\delta_{m,n+2} + \frac{2}{3} \delta_{m,n} + \delta_{m,n-2})$$

$$a(222|mn) = \frac{(-1)^n 2^{1/2} 3 \cdot 5^{5/2} (2m+1)(2n+1)n(n+1)}{7^{1/2} [(m+n+3)(m+n+1)(m+n-1)]^2} \quad (\text{B.9})$$

$$\times (m(2m+1) \delta_{m,n+2} - \frac{(2m+5)(2m-3)}{3} \delta_{m,n} + (m+1)(2m+1) \delta_{m,n-2})$$

$$a(224|mn) = \frac{(-1)^n 2^{1/2} \cdot 3^2 \cdot 5^{3/2} (n+2)! (2m+1)(2n+1)}{7^{1/2} (n-2)! [(m+n+3)(m+n+1)(m+n-1)]^2} \quad (\text{B.10})$$

$$\times (\delta_{m,n+2} + 4 \delta_{m,n} + \delta_{m,n-2})$$

$$a(202|mn) = \frac{(-1)^m 2 \cdot 5^{3/2} m(m+1)}{(2m+3)(2m-1)} \delta_{m,n} \quad (\text{B.11})$$

where  $\delta_{m,n}$  is the Kronecker delta function.

## CHAPTER 4

## ION, DIPOLE AND QUADRUPOLE MIXTURE

4.1 Introduction

A civilised model of an electrolyte is one in which the molecular nature of both the ions and solvent are treated on an equal basis. We take the solvent molecules to be hard spheres containing a point dipole and tetrahedral quadrupole, and the ions are charged hard spheres. This very simple model may be regarded as a fairly unsophisticated representation of an aqueous electrolyte. If the diameter of the ions and solvent molecules are the same,  $R$  say, then the model is said to be a Restricted Civilised Model.

As explained in Chapter 2, the correlation functions  $f$  describing this system, can be expanded using the set of orthogonal functions  $\phi_{\mu\nu}^{mnl}$ . The coefficients  $f_{\mu\nu}^{mnl}(r)$  are calculated using the O-Z equation with some closure. In this chapter, it is shown that if the closures chosen are the Mean Spherical Approximation (MSA) or Linearised Hypernetted Chain Approximation (LHNC), the techniques used to calculate the coefficients in the linear quadrupole system [23] can be simply modified to describe the tetrahedral quadrupole system.

The symmetry properties will also be used to simply modify the perturbation techniques. The perturbation techniques, being easier to



use, allow us to calculate properties such as the critical temperature without the large amount of calculation associated with integral equation methods.

Suppose there is a mixture of ionic species, of number density  $\rho_i$ ,  $i=1,2,\dots,n$  and one solvent species of number density  $\rho_s$ . The correlation functions are described using a matrix  $\underline{f}(= \underline{g}, \underline{h}, \underline{c})$  in which the  $(i,j)$  component is the correlation function  $f_{ij}$ , between species  $i$  and  $j$ . The density is described using a matrix  $\underline{\rho}$  with elements  $\rho_i \delta_{ij}$  with  $\rho_i$  being the density of the  $i$ th species.

In Chapter 2, it was shown that as a consequence of the symmetry of the interaction potential the coefficients of the correlation functions  $\underline{f}(= \underline{g}, \underline{h}, \underline{c})$  have the simple form

$$f_{\mu\nu}^{mnl}(r) = f_{\pm\mu \pm\nu}^{mnl}(r) \quad (4.1a)$$

$$\mu + \nu = -4, 0, 4 \quad (4.1b)$$

$$\mu, \nu \text{ even} \quad (4.1c)$$

If we only retain those rotational invariants occurring in the interaction potential or those needed to form a closed set under O-Z closure then the correlation functions  $\underline{f}$  can be written

$$f_{\underline{r}}(1,2) = \sum_S f_{\underline{r}}^{mnl}(r) \phi^{mnl}(\omega_1, \omega_2, \hat{\underline{r}})$$

where  $S$  consists of the set of rotational invariants

$$\Phi^{000} = \Phi_{00}^{000} \quad (4.2a)$$

$$\Phi^{101} = -\Phi^{011} = \Phi_{00}^{101} \quad (4.2b)$$

$$\Phi^{202} (= \Phi^{022}) = \Phi_{-20}^{202} + \Phi_{20}^{202} \quad (4.2c)$$

$$\Phi^{123} (= -\Phi^{213}) = \Phi_{0-2}^{123} + \Phi_{02}^{123} \quad (4.2d)$$

$$\Phi^{224} = \Phi_{22}^{224} + \Phi_{-22}^{224} + \Phi_{2-2}^{224} + \Phi_{-2-2}^{224} \quad (4.2e)$$

$$\Phi^{222} = \Phi_{22}^{222} + \Phi_{-22}^{222} + \Phi_{2-2}^{222} + \Phi_{-2-2}^{222} \quad (4.2f)$$

$$\Phi^{220} = \Phi_{22}^{220} + \Phi_{-22}^{220} + \Phi_{2-2}^{220} + \Phi_{-2-2}^{220} \quad (4.2g)$$

$$\Phi^{121} (= -\Phi^{211}) = \Phi_{02}^{121} + \Phi_{0-2}^{121} \quad (4.2h)$$

Here

$$f_{\mu\nu}^{mnl}(r) = f_{\mu\nu}^{mnl}(r) \quad (4.3)$$

$$\mu, \nu = \begin{cases} 0 \\ \pm 2 \end{cases} \quad \begin{matrix} m, n = 0, 1 \\ m, n = 2 \end{matrix}.$$

The problem is to calculate the coefficients  $f_{\mu\nu}^{mnl}(r)$ . To do this, the equations of section 2.5 need to be rewritten for mixtures.

## 4.2 O-Z equation

For a multicomponent mixture the O-Z equation has the form

$$h(1,2) = c(1,2) + \int d3 \, c(1,3) \, \rho(3) \, h(3,2) \quad . \quad (4.4)$$

Generalising the techniques of section 2.5 to mixtures, (4.4) can be written as

$$\begin{aligned} \tilde{h}_{\chi, \mu\nu}^{mn}(k) &= \tilde{c}_{\chi, \mu\nu}^{mn}(k) + \sum_{n', \mu'} \frac{1}{2n'+1} \tilde{c}_{\chi, \mu\mu'}^{mn'}(k) \\ &\quad \rho \tilde{h}_{\chi, \mu'v}^{n'n}(k) \quad . \end{aligned} \quad (4.5)$$

The definition of the transforms is a straightforward generalisation of those for the single component fluid.

For the ion-dipole-tetrahedral quadrupole mixture, symmetry allows the lower indices  $\mu, v$  to be suppressed in the style of (4.3). The set  $S$  of rotational invariants [eqn. (4.2)] is used so only the values  $m, n$  can take are 0, 1, 2.

For  $\chi = 2$ , (4.5) becomes

$$\begin{aligned} \tilde{h}_2^{22}(k) &= \tilde{c}_2^{22}(k) + \rho_{QT} \tilde{c}_2^{22}(k) \tilde{h}_2^{22}(k) \\ \text{where } \rho_{QT} &\equiv \frac{2\rho_S}{5} \quad . \end{aligned} \quad (4.6)$$

This equation which only describes quadrupole-quadrupole interactions between the solvent molecules has the appearance of an Ornstein-Zernike equation for a one-component fluid of density  $\rho_{QT}$ .

For  $\chi = 1$ , (4.5) becomes

$$\begin{aligned}\tilde{h}_1^{22}(k) &= \tilde{c}_1^{22}(k) + \rho_{Q_T} \tilde{c}_1^{22}(k) \tilde{h}_1^{22}(k) \\ &+ \rho_D \tilde{c}_1^{21}(k) \tilde{h}_1^{12}(k)\end{aligned}\quad (4.7a)$$

$$\begin{aligned}\tilde{h}_1^{21}(k) &= \tilde{c}_1^{21}(k) + \rho_{Q_T} \tilde{c}_1^{22}(k) \tilde{h}_1^{21}(k) \\ &+ \rho_D \tilde{c}_1^{21}(k) \tilde{h}_1^{11}(k)\end{aligned}\quad (4.7b)$$

$$\begin{aligned}\tilde{h}_1^{11}(k) &= \tilde{c}_1^{11}(k) + \rho_{Q_T} \tilde{c}_1^{12}(k) \tilde{h}_1^{21}(k) \\ &+ \rho_D \tilde{c}_1^{11}(k) \tilde{h}_1^{11}(k)\end{aligned}\quad (4.7c)$$

where

$$\rho_D = \frac{\rho_S}{3} \quad . \quad (4.8)$$

These equations describe dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions between solvent molecules, and take the form of the O-Z equation for a 2-component mixture where the density of the components are  $\rho_{Q_T}$  and  $\rho_D$ . The equations for  $\chi = 0$  are similar but too cumbersome to list explicitly. The equations for an ion-dipole-linear quadrupole system are identical provided  $\rho_{Q_T}$  is replaced by  $\rho_{Q_L} = \frac{\rho_S}{5}$ .

Finally we write the closures for the system. The exact hard core condition implies

$$\begin{aligned} h^{000}(r) &= -1, \quad r < R \\ h^{mnl}(r) &= 0, \quad r < R \quad \text{all other } (mnl) \end{aligned} \quad (4.9)$$

In the MSA we have

$$c^{mnl}(r) = -\beta u^{mnl}(r), \quad r > R \quad (4.10)$$

and in the LHNC

$$c^{000}(r) = \beta u^{000}(r) + h^{000}(r) - \ln(1 + h^{000}(r)) \quad r > R \quad (4.11)$$

and for  $(mnl) \neq (000)$

$$c^{mnl}(r) = -\beta u^{mnl}(r) + \left( \frac{h^{000}(r)}{1 + h^{000}(r)} \right) h^{mnl}(r) \quad r > R. \quad (4.12)$$

These equations are the same as for the linear quadrupole. The only feature distinguishing the two systems is the expression used for  $\mu^{mnl}$ . However if the term  $\Theta_T$  in the expressions for  $u^{224}$ ,  $u^{123}$  and  $u^{022}$  (2.25-2.27) is replaced by  $(3/2)^{1/2} \Theta_L$ , the equations for both systems are identical. Consequently existing programs which solve the LHNC equations for an ion-dipole-linear quadrupole mixture only require the above minor modification to handle an ion-dipole-tetrahedral quadrupole mixture.

### 4.3 Tetrahedral Quadrupole Fluid in the MSA

As an example of the application of the results of the previous section we consider the MSA solution for a fluid consisting of hard spheres (diameter  $R$ , density  $\rho$ ) with embedded point tetrahedral quadrupoles of magnitude  $\Theta_T$ . The solution of the Ornstein-Zernike equation for this problem can be written in terms of four rotational invariants:  $\phi^{000}$ ,  $\phi^{220}$ ,  $\phi^{222}$  and  $\phi^{224}$ . Hence only four independent functions of  $r$  are needed:  $h^{000}(r)$  and  $h^{221}(r)$ ,  $l = 0, 2, 4$ . From (4.5) we see that one of these functions obeys the equation (in  $k$ -space)  $\chi = 0$ ,  $m=n=0$

$$\tilde{h}^{000}(k) = \tilde{c}^{000}(k) + \rho \tilde{c}^{000}(k) \tilde{h}^{000}(k) \quad (4.13)$$

$$\tilde{h}^{000}(k) = h_0^{00}(k) \quad (4.14a)$$

$$\tilde{c}^{000}(k) = \tilde{c}_0^{00}(k). \quad (4.14b)$$

The boundary conditions for (4.13) are

$$\begin{aligned} h^{000}(r) &= -1, \quad r < R, \\ c^{000}(r) &= 0, \quad r > R, \end{aligned} \quad (4.15)$$

so that (4.13) is just the Percus-Yevick equation for hard spheres, which has a known solution [1].

For the remaining three functions  $h_{\mu\nu}^{22\ell}(r)$ ,  $\ell = 0, 2, 4$ , we have from (4.5)

$$\tilde{h}_\chi(k) = \tilde{c}_\chi(k) + \frac{2\rho}{5} \tilde{c}_\chi^*(k) \tilde{h}_\chi(k), \quad \chi = 0, 1, 2, \quad (4.16)$$

where

$$\tilde{h}_\chi(k) \equiv (-1)^\chi \sum_{l=0,2,4} \begin{pmatrix} 2 & 2 & l \\ \chi & -\chi & 0 \end{pmatrix} \tilde{h}^{22l}(k), \quad (4.17)$$

with a similar definition for  $\tilde{c}_\chi(k)$ . The boundary conditions for (4.16)

$$h^{22l}(r) = 0, \quad r < R, \quad l = 0, 2, 4, \quad (4.18)$$

$$c^{220}(r) = c^{222}(r) = 0, \quad r > R, \quad (4.19)$$

$$c^{224}(r) = -2(70)^{1/2} \beta \theta_T^2 r^{-5}, \quad r > R. \quad (4.20)$$

Equations (4.13) and (4.16) can be solved by Baxter's Wiener-Hopf factorization method [2] in which  $\tilde{c}_\chi(k)$  with well defined analytic properties

$$\tilde{c}_\chi(k) = \tilde{q}_\chi(k) + \tilde{q}_\chi(-k) - \frac{2\rho}{5} \tilde{q}_\chi(k) \tilde{q}_\chi(-k), \quad (4.21)$$

$$\tilde{h}_\chi = \tilde{q}_\chi(k) + \frac{2\rho}{5} \tilde{q}_\chi(k) \tilde{h}_\chi(k). \quad (4.22)$$

We proceed as in [3] by defining one dimensional inverse  $F_\chi(r)$

$$F_{\chi}(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp(-ikr) \hat{f}_{\chi}(k) \quad (f = h, c \text{ or } q) \quad (4.23)$$

so that (4.21) and (4.22) become

$$C_{\chi}(r) = Q_{\chi}(r) - \frac{2\rho}{5} \int_0^{\infty} Q_{\chi}(r+s) Q_{\chi}(s) ds, \quad (4.24)$$

$$H_{\chi}(r) = Q_{\chi}(r) = \frac{2\rho}{5} \int_0^{\infty} Q_{\chi}(s) H_{\chi}(r-s) ds. \quad (4.25)$$

From Appendix 2.4 and (4.23) it follows that ( $F = H, C$  or  $Q$ )

$$F_{\chi}(r) = 2\pi(-1)^{\chi} \sum_{\ell=0,2,4} \begin{pmatrix} 2 & 2 & \ell \\ \chi & -\chi & 0 \end{pmatrix} \int_{|r|}^{\infty} ds s P_{\ell}\left(\frac{r}{s}\right) f^{22\ell}(s), \quad (4.26)$$

where  $P_{\ell}(x)$  is a Legendre polynomial of degree  $\ell$ .

The large  $r$  behaviour of  $Q_{\chi}(r)$  can be found from the boundary conditions on  $C_{\chi}(r)$  using (4.18) - (4.20), however, for an ion-dipole-quadrupole mixture the asymptotic behaviour of  $Q_{\chi}(r)$  at large  $r$  can be obtained by considering the singularity at  $k = 0$  in (4.21). For a tetrahedral quadrupolar fluid the only contribution to  $C_{\chi}(r)$  for  $r > R$  is from  $c^{224}(r)$ . But since

$$\int_r^{\infty} ds s^{-1} P_{\ell}\left(\frac{r}{s}\right) = \frac{1}{2} \int_{-1}^1 dx x^{\ell-2} P_{\ell}(x) = 0, \quad \ell > 2, \quad (4.27)$$

we have from (4.19), (4.20) and (4.26)

$$C_{\chi}(r) = 0, \quad r > R \quad (\chi = 0, 1, 2) \quad (4.28)$$



and so

$$Q_{\chi}(r) = 0, \quad r > R \quad (\chi = 0, 1, 2). \quad (4.29)$$

For  $r < R$ , we see from (4.18) and (4.26) that  $H_{\chi}(r)$  is of the form

$$H_{\chi}(r) = H_{4\chi} r^4 + H_{2\chi} r^2 + H_{0\chi}, \quad r < R \quad (\chi = 0, 2, 4), \quad (4.30)$$

where the coefficients of this quartic polynomial are

$$\begin{aligned} H_{4\chi} &= \left(\frac{35}{8}\right) (-1)^{\chi} 2\pi \begin{pmatrix} 2 & 2 & 4 \\ \chi & -\chi & 0 \end{pmatrix} \int_R^{\infty} dr r^{-3} h^{224}(r), \\ H_{2\chi} &= (-1)^{\chi} 2\pi \begin{pmatrix} 3 \\ 2 \end{pmatrix} \begin{pmatrix} 2 & 2 & 2 \\ \chi & -\chi & 0 \end{pmatrix} \int_R^{\infty} dr r^{-1} h^{222}(r) \\ &\quad - \left(\frac{15}{4}\right) \begin{pmatrix} 2 & 2 & 4 \\ \chi & -\chi & 0 \end{pmatrix} \int_R^{\infty} dr r^{-1} h^{224}(r) \end{aligned} \quad (4.32)$$

$$\begin{aligned} H_{0\chi} &= (-1)^{\chi} 2\pi \begin{pmatrix} 2 & 2 & 0 \\ \chi & -\chi & 0 \end{pmatrix} \int_R^{\infty} dr rh^{220}(r) \\ &\quad - \frac{1}{2} \begin{pmatrix} 2 & 2 & 2 \\ \chi & -\chi & 0 \end{pmatrix} \int_R^{\infty} dr rh^{222}(r) \\ &\quad + \frac{3}{8} \begin{pmatrix} 2 & 2 & 4 \\ \chi & -\chi & 0 \end{pmatrix} \int_R^{\infty} dr rh^{224}(r) \end{aligned} \quad (4.33)$$

for  $\chi = 0, 2, 4$ , and we have to determine the values of the six

moments of  $h^{22\ell}(r)$  in (4.31) to (4.33). To do so, we use the inverse transformation of (4.26) \*

$$2\pi c^{22\ell}(r) = (2\ell + 1) \sum_{|\chi|=0}^2 (-1)^\chi \begin{pmatrix} 2 & 2 & \ell \\ \chi & -\chi & 0 \end{pmatrix} \left( -\frac{1}{r} C'_\chi(r) + \frac{P'_\ell(1)}{r^2} C_\chi(r) - \frac{1}{r^3} \int_0^r ds P''_\ell\left(\frac{s}{r}\right) C_\chi(s) \right), \quad \ell = 0, 2, 4 \quad (4.34)$$

which because of (4.28) becomes, for  $r > R$

$$2\pi c^{22\ell}(r) = -\frac{(2\ell + 1)}{r^3} \sum_{|\chi|=0}^2 (-1)^\chi \begin{pmatrix} 2 & 2 & \ell \\ \chi & -\chi & 0 \end{pmatrix} \int_0^R ds P''_\ell\left(\frac{s}{r}\right) C_\chi(s), \quad r > R. \quad (4.35)$$

Using the boundary conditions, (4.19) and (4.20) we can equate coefficients of  $r^{-n}$  to obtain three equations for the six moments of  $h^{22\ell}(r)$

$$0 = \sum_{|\chi|=0}^2 (-1)^\chi \begin{pmatrix} 2 & 2 & 2 \\ \chi & -\chi & 0 \end{pmatrix} \int_0^R ds C_\chi(s), \quad (4.36)$$

$$0 = \sum_{|\chi|=0}^2 (-1)^\chi \begin{pmatrix} 2 & 2 & 4 \\ \chi & -\chi & 0 \end{pmatrix} \int_0^R ds C_\chi(s), \quad (4.37)$$

$$2\pi[2(70)^{1/2} \beta \theta_T^2] = 9\left(\frac{105}{2}\right) \sum_{|\chi|=0}^2 (-1)^\chi \begin{pmatrix} 2 & 2 & 4 \\ \chi & -\chi & 0 \end{pmatrix} \int_0^R ds s^2 C_\chi(s). \quad (4.38)$$

Three other equations for the six moments can be obtained from the fact that  $Q_\chi(r)$  is continuous at  $r = R$ , that is

$$Q_\chi(R) = 0, \quad \chi = 0, 2, 4. \quad (4.39)$$

The remaining task is to relate the constants  $H_{i\chi}$  ( $i=0,2,4$ ) to the integrals of  $C_\chi$  in (4.36) - (4.38). We observe from (4.25) that since  $H_\chi(r)$  is a quartic polynomial in  $r$  for  $r < R$ ,  $Q_\chi(r)$  must also be a quartic polynomial for  $r < R$ . This polynomial can be specified in terms of its four moments

$$M_{i\chi}(H_{4\chi}, H_{2\chi}, H_{0\chi}) \equiv \int_0^R ds s^i Q_\chi(s), \quad i = 0, 1, 2, 3, \quad (4.40)$$

which can in turn be related to the constants  $H_{i\chi}$  ( $i = 0, 2, 4$ ) using (4.25) and (4.30). Finally, using (4.24), we have the desired results

$$\int_0^R ds C_\chi(s) = M_{0\chi} - \frac{\rho}{5} M_{0\chi}^2 \quad (4.41)$$

and

$$\int_0^R ds s^2 C_\chi(s) = M_{2\chi} + \frac{2\rho}{5} (M_{1\chi}^2 - M_{0\chi} M_{2\chi}) \quad (4.42)$$

for the right hand-side of (4.36) - (4.38).

The MSA solution of a hard sphere tetrahedral quadrupole fluid has been reduced to solving a set of coupled algebraic equations,

(4.36) - (4.42) for the three constants  $H_{i\chi}$  ( $i = 0, 2, 4$ ). For instance, the excess <sup>internal</sup> free energy per particle over the hard sphere reference system is

$$\begin{aligned} \beta U^{\text{ex}} / N &= \frac{16(70)^{1/2} \pi \beta \rho \Theta_T^2}{225R^5} \int_R^\infty ds s^{-3} h_{\mu\nu}^{224}(s) \\ &= \frac{64(70)^{1/2} \beta \rho \Theta_T^2}{875R^5} \sum_{|\chi|=0}^2 (-1)^\chi \begin{pmatrix} 2 & 2 & 4 \\ \chi & -\chi & 0 \end{pmatrix} H_4 \chi. \end{aligned} \quad (4.43)$$

Also, once  $Q_\chi(r)$  is known, the total correlation function can be determined from .

A comparison between the usefulness of the transformation given by (4.23) which was also used in [3] and [4], and that used in [5] and [6] is given in Appendix 2.4.

#### 4.4 Thermodynamic Perturbation Theory

Perturbation techniques have been applied to molecular fluids, ionic, dipolar fluids, linear quadrupoles and polarizable fluids as well as combinations of these [7-20]. Perturbation techniques based on the Pople expansion and the Padé approximants thereof, are relatively easy to use and provides good results for the free energy and details of the phase diagram. It is difficult and time-consuming to use the integral equation methods to calculate phase diagrams and even then the results seem disappointing compared to the perturbation schemes [9,21]. For this reason it is useful to extend the perturbation techniques so they can describe systems of hard spheres imbedded with dipoles and tetrahedral quadrupoles. We briefly

outline the derivation.

Consider a system for which the Hamiltonian is of the form

$$H_{\lambda} = H_0 + \lambda V, \quad (4.44)$$

where  $H_0$  is the hamiltonian of a suitably chosen reference system,  $V$  is the perturbation potential and the coupling constant  $\lambda$  provides a means by which we can keep track of the order of the perturbation. The excess free energy of the system at state  $\lambda$  relative to the reference state  $\lambda = 0$  is given by the identity due to Pauli

$$F_{\lambda}^{\text{ex}} \equiv F_{\lambda} - F_0 = \int_0^{\lambda} d\lambda' \frac{\partial F(\lambda')}{\partial \lambda'}, \quad (4.45)$$

where

$$\beta F(\lambda) = \ln \left\{ \frac{1}{N!} \int d\mathbf{l} \cdots d\mathbf{N} \exp(-\beta H_0) \exp(-\lambda \beta V) \right\}. \quad (4.46)$$

The result we want is obtained by setting  $\lambda = 1$ . Combining (4.45) and (4.46) we obtain the general expansion

$$\begin{aligned} F_{\lambda}^{\text{ex}} = & \lambda \langle V \rangle_0 + \frac{1}{2} \lambda^2 \beta [\langle V \rangle_0^2 - \langle V^2 \rangle_0] \\ & + \frac{1}{3} \lambda^3 \beta (\langle V \rangle_0^3 - \frac{3}{2} \langle V \rangle_0 \langle V^2 \rangle_0 + \frac{1}{2} \langle V^3 \rangle_0) + O(\lambda^4), \end{aligned} \quad (4.47)$$

where

$$\langle V^n \rangle_0 \equiv \frac{\int d\mathbf{l} \dots d\mathbf{N} V^n \exp(-\beta H_0)}{\int d\mathbf{l} \dots d\mathbf{N} \exp(-\beta H_0)}, \quad n = 1, 2, 3 \quad (4.48)$$

is the expectation value taken with respect to the reference Hamiltonian.

If the intermolecular potential in the reference system is independent of the molecular orientations and the perturbation potential  $V$  is a pair wise sum of multipolar potentials, we have

$$\langle V \rangle_0 = 0 \quad (4.49)$$

because of the angular integrations. Consequently (4.47) simplifies to

$$F_{\lambda}^{\text{ex}} = -\frac{1}{2} \lambda^2 \beta \langle V^2 \rangle_0 + \frac{1}{6} \lambda^3 \beta^2 \langle V^3 \rangle_0 + O(\lambda^4). \quad (4.50)$$

For most reasonable values of the multipole moments (4.50) shows no sign of convergence. However, it has been found that a Padé approximant formed by treating the right-hand side of (4.50) as the first two terms of a geometric series in  $\lambda$

$$F_{\lambda, \text{Padé}} = \frac{-\frac{1}{2} \lambda^2 \beta \langle V^2 \rangle_0}{1 + \frac{1}{3} \lambda \beta (\langle V^3 \rangle_0 / \langle V^2 \rangle_0)} \quad (4.51)$$

provides remarkably good descriptions of the properties of dipolar hard spheres [22] and dipole-linear quadrupolar hard sphere fluids [23]. This serendipitous construction is motivated by intuitions

based upon a study of the MSA result for dipolar fluids and upon Onsager's observation that the ground state energy must be linear in the coupling constant [10,24,25].

The remaining task is to obtain expressions for the expectation values of the perturbation potential  $\langle V^2 \rangle_0$  and  $\langle V^3 \rangle_0$ . For a fluid of hard spheres with embedded dipoles and linear quadrupoles the perturbation potential is of the form

$$\begin{aligned} V &= \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} U(i,j) \\ &= \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} (U_{DD}(i,j) + U_{DQ_L}(i,j) + U_{Q_L Q_L}(i,j)), \end{aligned} \quad (4.52)$$

where the dipole-dipole  $U_{DD}$ , dipole-quadrupole  $U_{DQ_L}$  and quadrupole-quadrupole  $U_{Q_L Q_L}$  potentials are given by (2.19), (2.21) and (2.22). Combining (4.48), (4.52) and the expressions for the pair potentials we find

$$\begin{aligned} \langle V^2 \rangle_0 &= \frac{1}{2} \left( \frac{\rho}{8\pi^2} \right)^2 \int d\mathbf{l} \, d\mathbf{2} \, g_0^{(2)}(1,2) \{ U_{DD}^2(1,2) + 2U_{DQ_L}^2(1,2) + U_{Q_L Q_L}^2(1,2) \} \\ &= \left( \frac{N}{\beta^2} \right) \rho^* \left( \frac{1}{3} \mu^{*4} I_6 + \mu^{*2} \Theta_L^{*2} I_8 + \frac{7}{5} \Theta_L^{*4} I_{10} \right), \end{aligned} \quad (4.53)$$

$$\begin{aligned} \langle V^3 \rangle_0 &= \frac{1}{4} \left( \frac{\rho}{8\pi^2} \right)^2 \int d\mathbf{l} \, d\mathbf{2} \, g_0^{(2)}(1,2) \{ 3U_{DD}^2(1,2)U_{Q_L Q_L}(1,2) \\ &\quad + 6U_{DD}(1,2)U_{DQ_L}^2(1,2) + 6U_{Q_L Q_L}(1,2)U_{DQ_L}^2(1,2) + U_{DD}(2,3)U_{DD}(3,1) \} \end{aligned}$$

$$\begin{aligned}
& + \frac{3}{4} \left( \frac{\rho}{8\pi} \right)^3 \int d1 d2 d3 g_0^{(3)}(1,2,3) \{ U_{DD}(1,2) U_{DD}(2,3) U_{DD}(3,1) \\
& + 3 U_{DD}(1,2) U_{DQ_L}(2,3) U_{Q_L D}(3,1) \\
& + 3 U_{DQ_L}(1,2) U_{Q_L Q_L}(2,3) U_{Q_L D}(3,1) \\
& + U_{Q_L Q_L}(1,2) U_{Q_L Q_L}(2,3) U_{Q_L Q_L}(3,1) \} \\
& = \left( \frac{6N}{\beta} \right) \rho^{*2} (2 \mu^{*4} \Theta_L^{*2} I_{11} + \frac{12}{7} \mu^{*2} \Theta_L^{*4} I_{13} + \frac{36}{49} \Theta_L^{*6} I_{15}) \\
& + \left( \frac{6N}{5\beta^3} \right) \rho^{*2} \left( \frac{\mu^{*6}}{54} I_{DDD} + \frac{\mu^{*4} \Theta_L^{*2}}{480} I_{DDQ} \right. \\
& \quad \left. + \frac{\mu^{*2} \Theta_L^{*4}}{640} I_{DQQ} + \frac{\Theta_L^{*6}}{6400} I_{QQQ} \right). \quad (4.54)
\end{aligned}$$

In the above results  $g_0^{(2)}$  and  $g_0^{(3)}$  are respectively, the pair and triplet distribution function of the reference system. We see that to order  $\lambda^3$  there are two and three body contributions to  $\langle V^3 \rangle_0$ .

The dimensionless quantities have the following definitions

$$\begin{aligned}
\rho^* &= \rho R^3, \\
\mu^{*2} &= \beta \mu^2 / R^3, \\
\Theta_L^{*2} &= \beta \Theta_L^2 / R^5,
\end{aligned} \quad (4.55)$$

where  $R$  is the hard sphere diameter and  $\rho$  is the number density.



The quantities  $I_n$  and  $I_{\alpha\beta\gamma}$  are defined by

$$I_n = 4\pi \int_0^\infty dr r^{2-n} g_0^{(2)}(r) , \quad (4.56)$$

$$I_{\alpha\beta\gamma} = \int dr ds g_0^{(3)}(r,s) W_{\alpha\beta\gamma}(r,s) \quad (4.57)$$

where  $W_{\alpha\beta\gamma}$  is the three body potential function found in the theory of dispersion forces [26].

We now give the results for  $\langle V^2 \rangle_0$  and  $\langle V^3 \rangle_0$  for the case of hard spheres plus dipoles and tehradral quadrupoles for which the dipole-quadrupole  $U_{DQ_T}$  and quadrupole-quadrupole  $U_{Q_T Q_T}$  potentials are given by (2.25)-(2.27). Using these expressions in (4.48) and (4.52) we get

$$\begin{aligned} \langle V^2 \rangle_0 &= \frac{1}{2} \left( \frac{\rho}{8\pi^2} \right)^2 \int d1 d2 g_0^{(2)}(1,2) \{ U_{DD}^2(1,2) + 2U_{DQ_T}^2(1,2) + U_{Q_T Q_T}^2(1,2) \} \\ &= \left( \frac{2N}{3\beta^2} \right) \rho^* \left( \frac{1}{2} \mu^{*4} I_6 + 2\mu^{*2} \Theta_T^{*2} I_8 + \frac{56}{15} \Theta_T^{*4} I_{10} \right) \end{aligned} \quad (4.58)$$

and

$$\begin{aligned} \langle V^3 \rangle_0 &= \frac{3}{4} \left( \frac{\rho}{8\pi^2} \right)^3 \int d1 d2 d3 g_0^{(3)}(1,2,3) \{ U_{DD}(1,2) U_{DD}(2,3) U_{DD}(3,1) \\ &\quad + 3U_{DD}(1,2) U_{DQ_T}(2,3) U_{Q_T D}(3,1) \\ &\quad + 3U_{DQ_T}(1,2) U_{Q_T Q_T}(2,3) U_{Q_T D}(3,1) \\ &\quad + U_{Q_T Q_T}(1,2) U_{Q_T Q_T}(2,3) U_{Q_T Q_T}(3,1) \} \end{aligned}$$

$$\begin{aligned}
= \left(\frac{6N}{\beta^3}\right) \rho^{*2} & \left( \frac{\mu^{*6}}{54} I_{DDD} + \frac{\mu^{*4} \Theta_T^{*2}}{360} I_{DDQ} \right. \\
& \left. + \frac{\mu^{*2} \Theta_T^{*4}}{360} I_{DQQ} + \frac{\Theta_T^{*6}}{2700} I_{QQQ} \right). \quad (4.59)
\end{aligned}$$

On comparing (4.54) and (4.59) we see that only three body terms contribute to  $\langle V^3 \rangle_0$  for the dipole-tetrahedral quadrupole system.

To obtain numerical results we must specify the reference system. A fluid of hard spheres at the same density and diameter is the obvious candidate. For the hard sphere reference system, the integrals  $I_n$  and  $I_{\alpha\beta\gamma}$  are only functions of the density and simple accurate representations of these functions have been compiled [25]. We now proceed to study two cases: a pure tetrahedral quadrupolar fluid and a dipole-tetrahedral quadrupolar fluid.

Consider first a pure tetrahedral quadrupolar fluid for which the results from thermodynamic perturbation theory can be obtained setting  $\mu^* = 0$  in (4.58) and (4.59). In figure 4.1 we compare the excess free energy,  $F^{ex}$ , obtained from the series expansion, including terms of order  $\lambda^3$ , (4.50) with that obtained from using the Padé approximant,  $F_{Padé}^{ex}$ , (4.51). The close agreement between the two results in the range  $0 < \Theta_T^{*2} < 1$  indicates that in this regime terms of order  $\lambda^3$  and higher are relatively unimportant. We note that  $\Theta_T^{*2}$  for water at room temperature is 0.62. In figure 4.2 we compare the internal energy obtained from the MSA, (4.43), with that obtained from the perturbation theory by differentiating the Padé free energy,  $F_{Padé}^{ex}$ , (4.51). The disagreement between the two theories is not unexpected since the MSA is essentially

equivalent to replacing the distribution functions  $g_0^{(2)}$  and  $g_0^{(3)}$  required in the perturbation theory by unit step functions [10]. It is interesting to note that the two body term of order  $(\lambda \theta_T^{*6})$  in  $\langle V^3 \rangle_0$  which is omitted in the MSA, turns out to be zero for

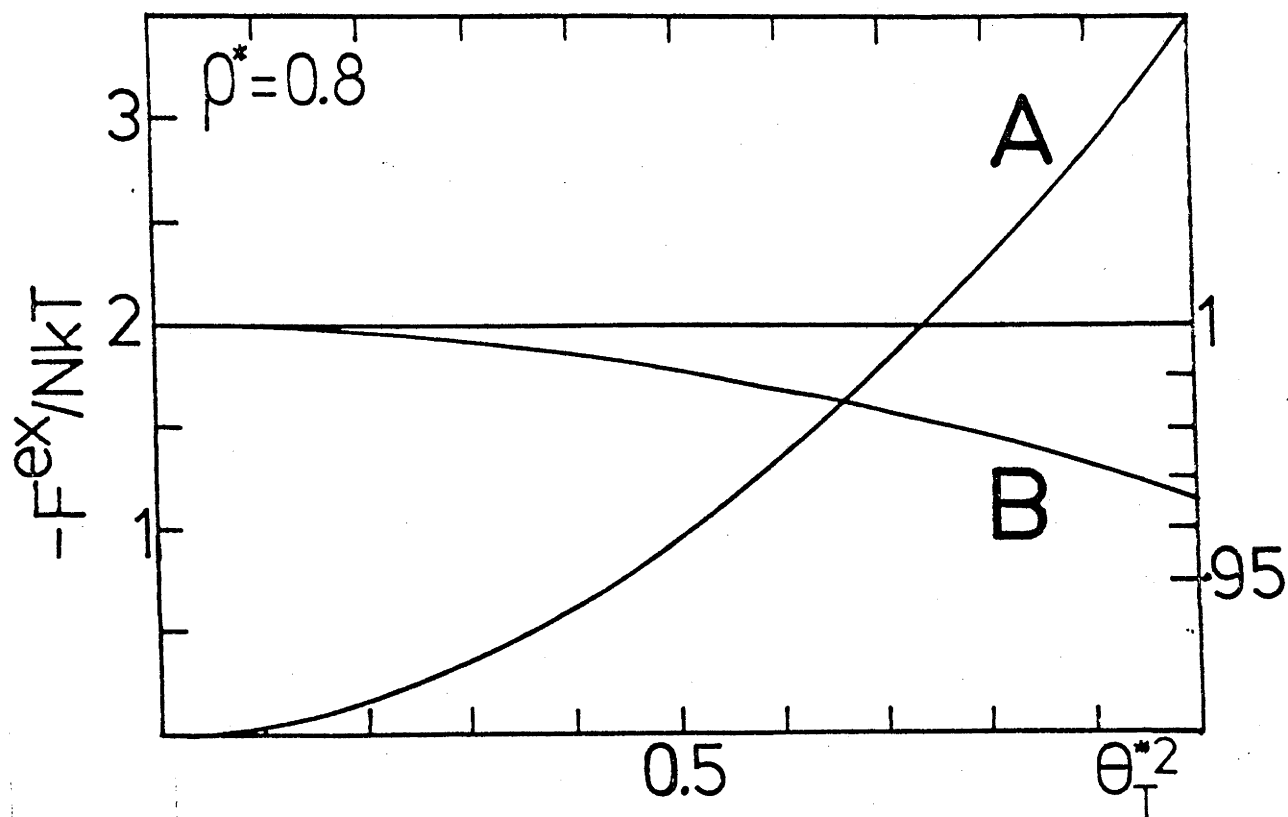


Fig. 4.1 Excess Free Energy per molecule at  $\rho^* = 0.8$  from perturbation theory (A)  $F_{PADE}^{ex}$  (left-hand scale), (B) The ratio  $(F_{series}^{ex}/F_{Pade}^{ex})$  (right-hand scale).

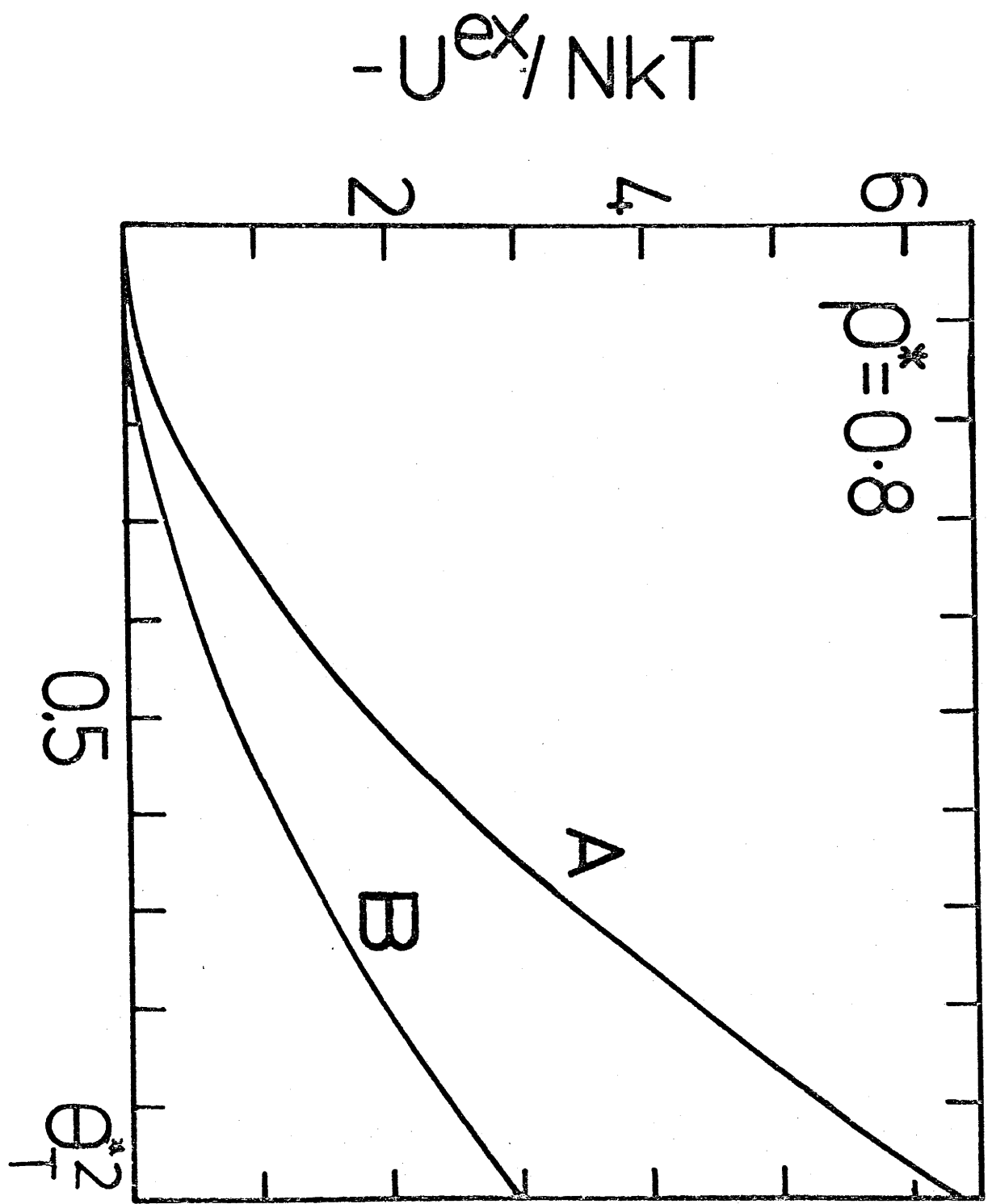


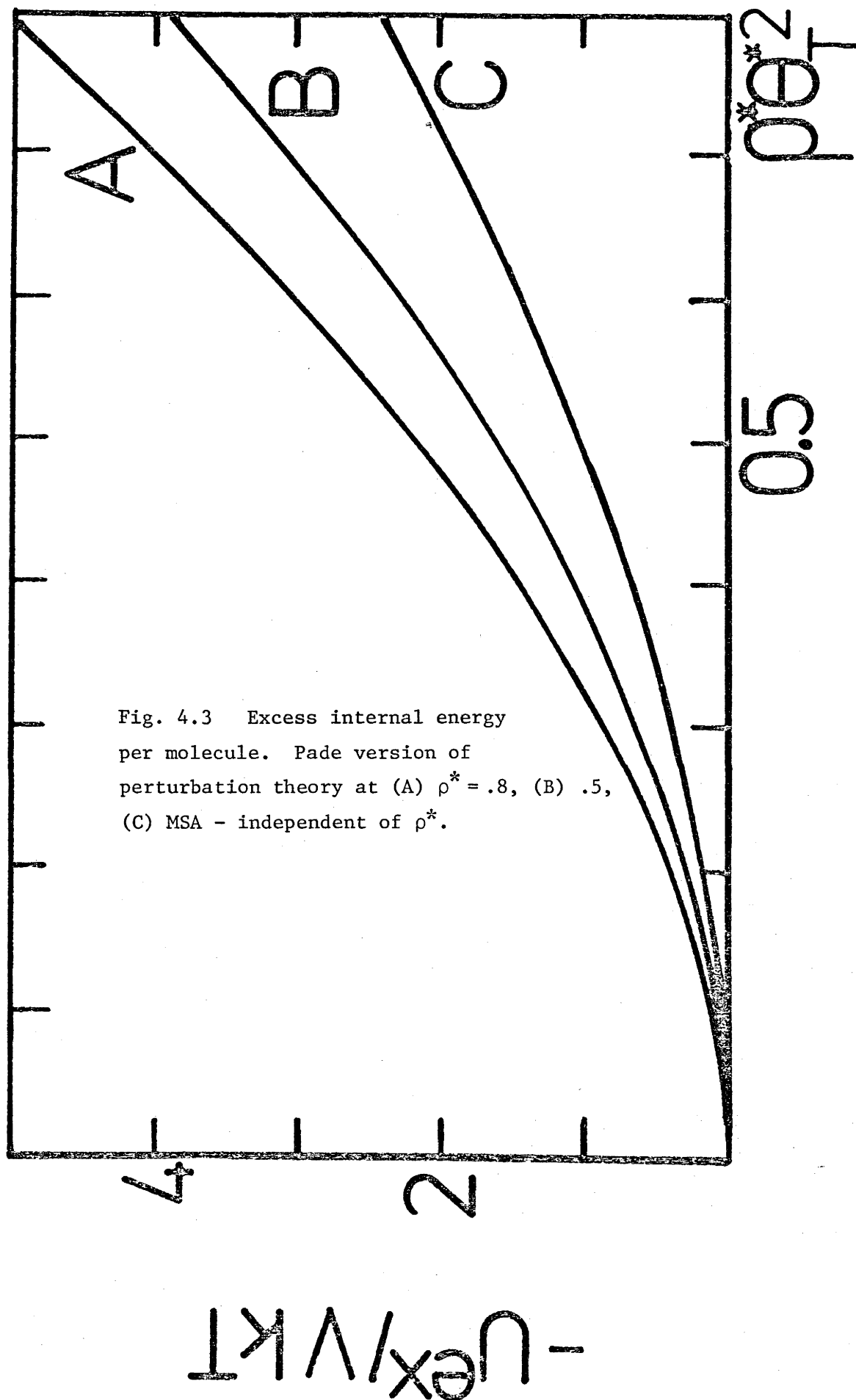
Fig. 4.2 Excess internal energy per molecule (A) Pade (B) MSA.

tetrahedral quadrupoles. In the MSA the internal energy per unit volume is only a function of the product  $(\rho^* \Theta_T^{*2})$ . This is not true in general. In figure 4.3 we compare the universal curve from the MSA with the Padé internal energy at different densities. The Padé and MSA results coincide only for  $\rho^* \ll 1$ .

We now turn to the case of a dipole-tetrahedral quadrupolar hard sphere fluid. We have chosen for our input data

$$\begin{aligned}\mu &= 1.84 \times 10^{-18} \text{ e.s.u.-cm} , \\ \Theta_T &= 2.5 \times 10^{-26} \text{ e.s.u.-cm}^2 , \\ R &= 3 \text{ \AA} ,\end{aligned}\tag{4.60}$$

which to a good approximation, are the dipole and tetrahedral quadrupole moments of water. Unlike the case of pure tetrahedral quadrupoles, there is considerable difference between the Padé (4.51) and series expansion (4.50) of the free energy (figure 4.4). It is obvious that this is due to the presence of the dipolar contribution. Hereafter we shall use the Padé version of the perturbation theory because it gives quite reasonable agreement with Monte Carlo results for the dipole-linear quadrupole hard sphere fluid [23]. In figures (4.5) - (4.7) we show the excess free energy, excess internal energy and the excess compressibility factor  $(\beta P^{\text{ex}}/\rho)$  as a function of temperature. The latter two properties are obtained by appropriate differentiations of the Padé free energy. By comparison with the curves obtained by setting  $\mu^* = 0$  or  $\Theta_T^* = 0$  we can see that the dipole-quadrupole interaction gives an important contribution to the



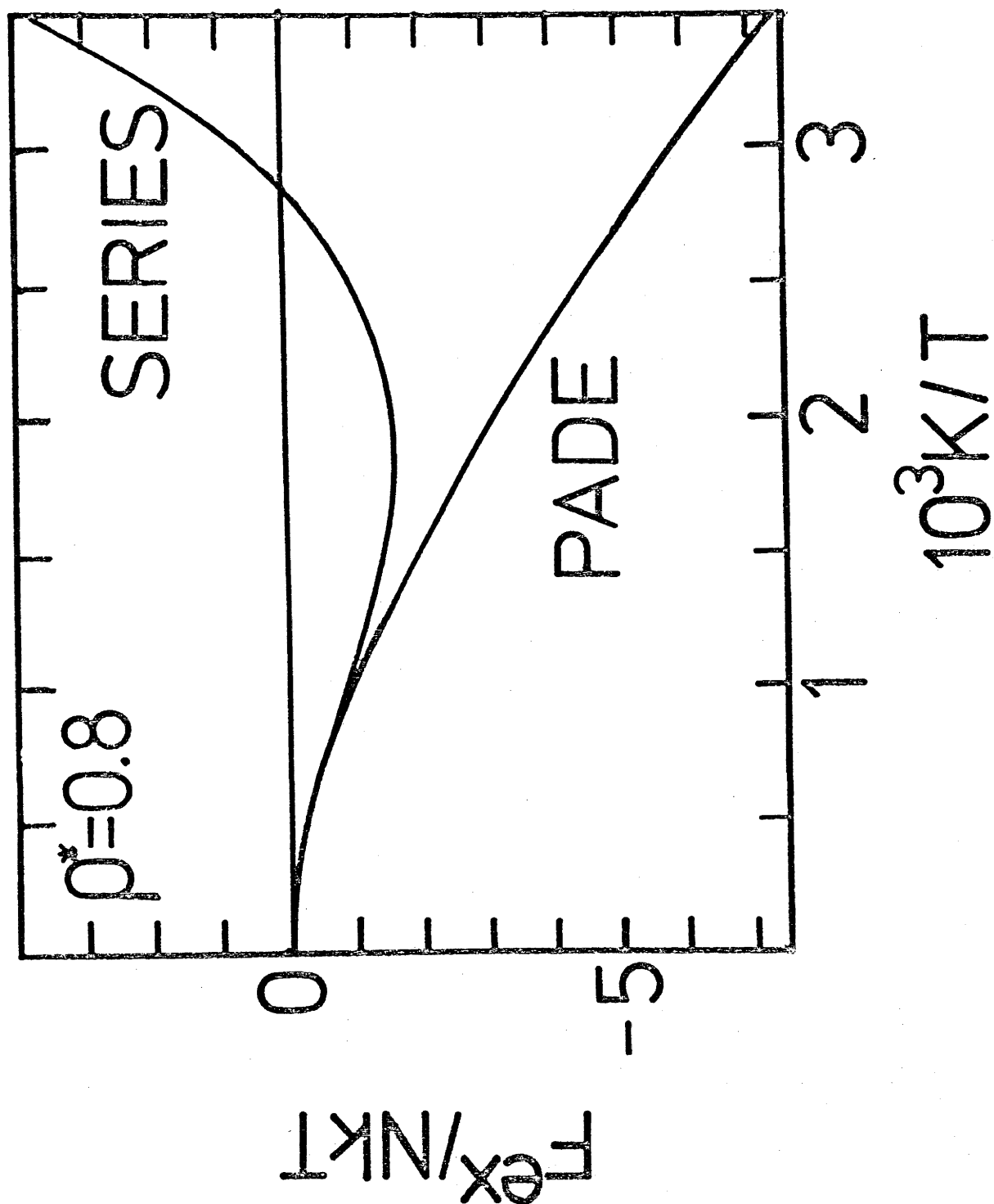


Fig. 4.4 Excess Free Energy per molecule for a dipole-quadrupolar hard sphere fluid at  $\rho^* = 0.8$  (water parameters), obtained from perturbation theory.

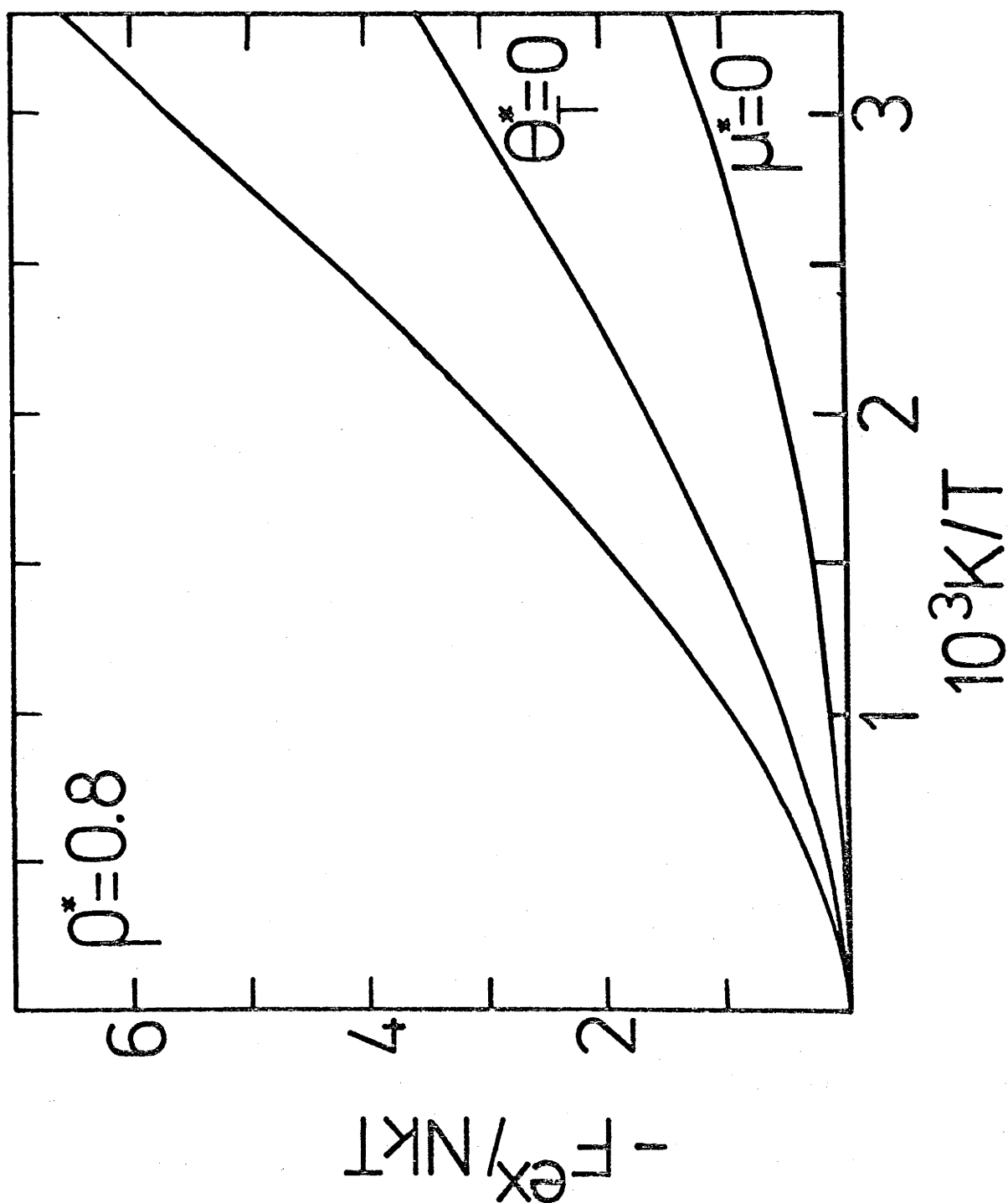


Fig. 4.5 Excess Free Energy per molecule of a dipole-tetrahedral quadrupolar fluid at  $\rho^* = .8$ . (water parameters used)  
 Pure tetrahedral quadrupolar fluid ( $\mu^* = 0$ ) and a pure dipolar fluid ( $\theta^* = 0$ ) also shown.



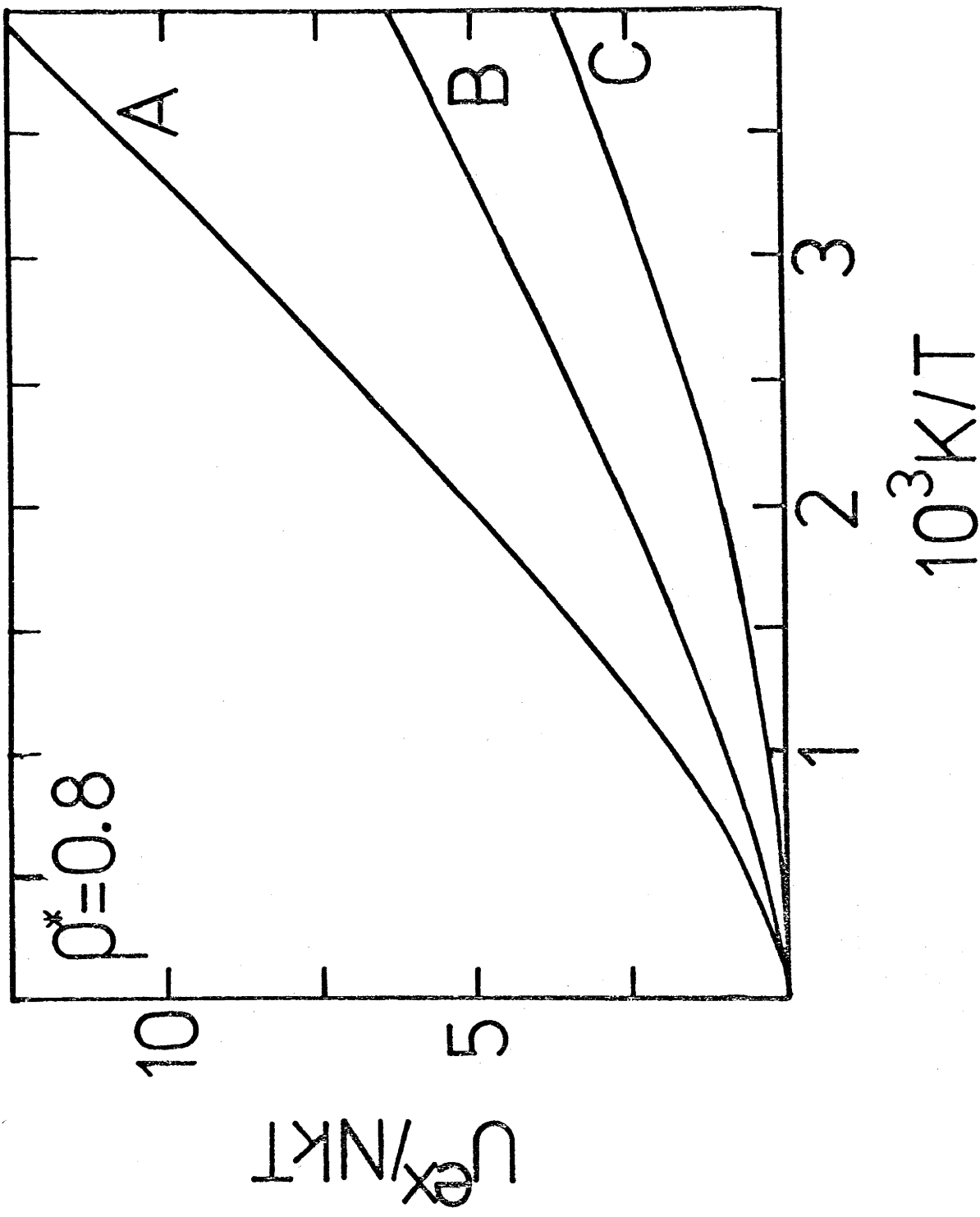


Fig. 4.6 Excess internal energy per molecule (A) dipole+quadrupole (B) dipole only (C) tetrahedral quadrupole.

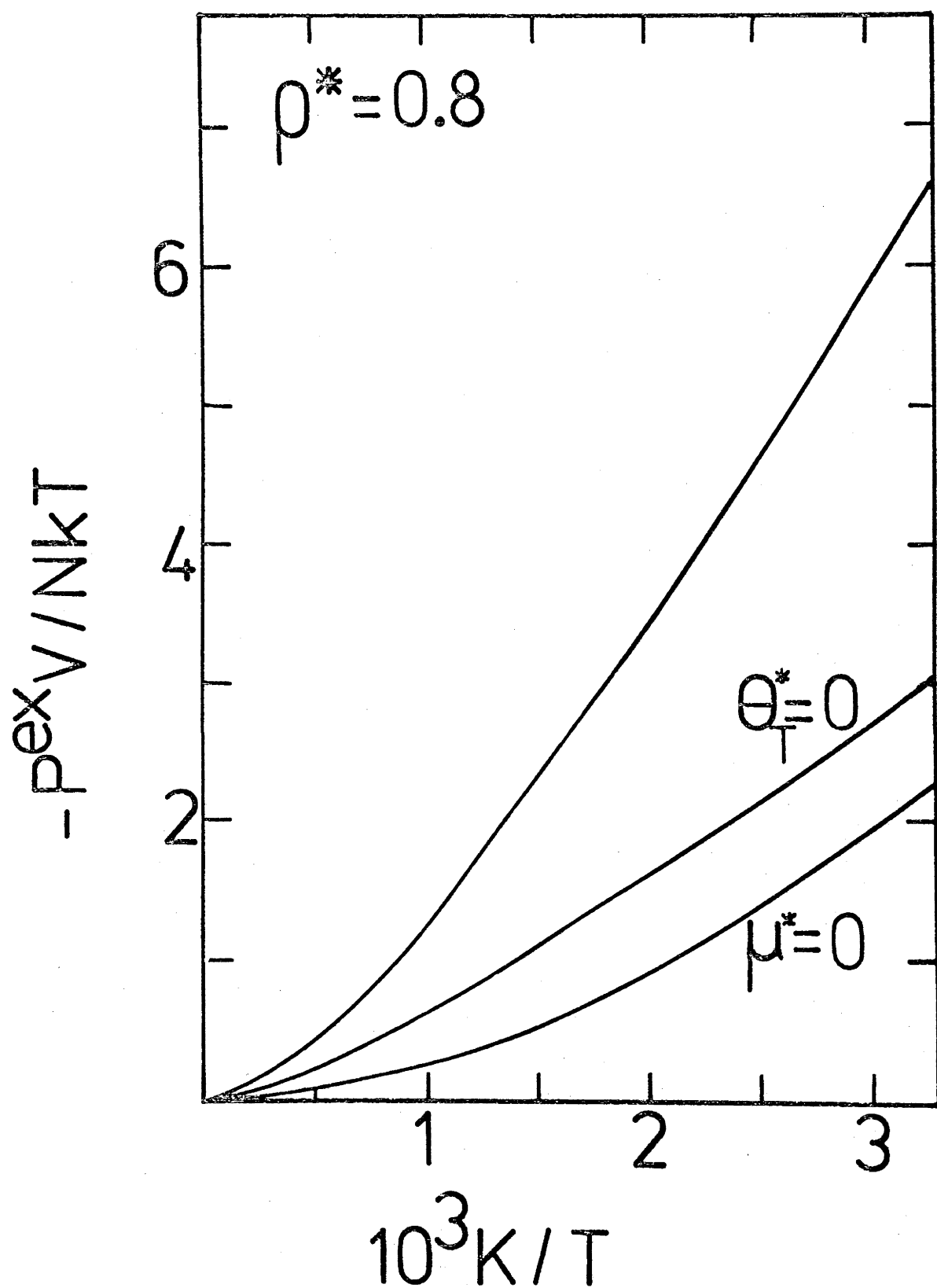


Fig. 4.7 Excess compressibility factor for dipole-tetrahedral quadrupolar hard sphere fluid at  $\rho^* = 0.8$ . (water parameters used) Results for pure dipolar and pure quadrupolar fluid shown.

thermodynamic properties of such fluids. We note that at  $\rho^* = 0.8$  ( $\beta P^{\text{ex}}/\rho$ ) for water-like values of  $\mu^*$  and  $\Theta_T^*$  is  $-6.6$  at room temperature. This almost cancels the reference value  $(\beta P_0/\rho) = 7.74$  for a hard sphere system and gives a fairly low pressure at room temperature. The water molecule is not 'hard' and not a sphere. Thus, the choice of the diameter becomes somewhat arbitrary, with  $3 \text{ \AA}$  usually being considered too high. For the purposes of showing the significance of the quadrupole on thermodynamic quantities it was a convenient size. For our calculation of the phase diagram we have chosen a diameter of  $2.7 \text{ \AA}$ . The hard-sphere reference system is assumed to be given by Carnahan-Starling equation of state. In table 4.1 we have listed some thermodynamic properties at the critical point for a pure dipolar and dipolar-quadrupolar fluid. While our simple model is not intended to reproduce the properties of water, we have nonetheless included water value in table 4.1 for comparison.

It must be said that Pople expansion and its extensions are theories applicable at "high" temperatures and densities and are therefore not expected to be accurate near the critical point. For a dipolar hard-sphere fluid, the thermodynamic perturbation theory yielded a reasonable value for the critical temperature but the critical densities and pressures were in error when compared with Monte Carlo results [9]. Thus our results for the critical behaviour for a dipole-tetrahedral quadrupole fluid can only be used to illustrate the relative importance of the dipole-quadrupole and quadrupole-quadrupole interaction in a water-like system.

TABLE 1

Properties of a dipole-tetrahedral quadrupole and a pure dipole hard-sphere fluid at the critical point (see eq. (18) for data)

	$T_c(k)$	$\rho_c$ ( $10^{22} \text{ cm}^{-3}$ )	$P_c$ ( $10^8 \text{ dyne/cm}^2$ )	$(P/\rho kT)_c$
dipole-quadrupole	609	1.27	3.86	0.362
dipole	358	0.83	1.31	0.324
water	647	1.09	2.20	0.226

Independently, Gubbins, Gray and Machado [19,20] developed TPT for general non-linear quadrupoles. The TPT for the tetrahedral quadrupole can be considered a special case, in which the symmetries reduce the amount of work.

#### 4.5 Conclusion

In this chapter, we have examined the statistical mechanics and thermodynamic properties of a system of molecules that contain a tetrahedral quadrupole moment. We have shown that in the MSA or LHNC treatment for ion-dipole-tetrahedral quadrupole systems, the solution to the Ornstein-Zernike equation can be obtained by trivial changes to existing programs [23] which have been designed to study similar

systems with linear quadrupoles. Preliminary studies using the thermodynamic perturbation theory suggest that dipole-quadrupole interactions in a water-like hard sphere dipole-tetrahedral quadrupolar fluid can be important.

Recently Carnie and Patey [27] have performed a number of calculations with the LHNC and QHNC closures for the polarizable ion-dipole-tetrahedral quadrupole system. For the QHNC closure, the simple transformation

$$\Theta_T \rightarrow \left(\frac{3}{2}\right)^{1/2} \Theta_L$$

is no longer sufficient, but the necessary modifications are not difficult. In a polarizable molecule, the local electric field distorts the molecular charge distribution and so changes its dipole moment. The molecule is said to have an 'effective' dipole  $\mu_{\text{eff}}$  which can be written as the sum of the permanent dipole  $\mu$  and the induced dipole  $\mu_{\text{ind}}$ . Polarizability is included in a 'mean field' sense, i.e. each molecule has the same induced dipole moment and so the same effective dipole moment  $\mu_{\text{eff}}$ .

The results are encouraging. When a moderate tetrahedral quadrupole is included the dielectric constant becomes independent of the closure (LHNC, QHNC and MSA). When water parameters are used, agreement is found with experimental values for the dielectric constant over a temperature range 25 C-300 C.

Since a hard sphere core is used, it is difficult to compare the calculated structure with experimental values. However, it is worth noting that the first minimum in  $g^{000}(r)$  occurs at 1.2 diameters (compares well with experimental results) and the second maximum occurs at 2 diameters (cf. 1.7 in experimental results).

These results justify the study of a system of hard spheres imbedded with dipoles and tetrahedral quadrupoles. If polarizability is included via an effective dipole moment, reasonable results are obtained for properties of water.

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## CHAPTER 5

## DIPOLES IN A FLUID

5.1 Introduction

Recently, Hayter and Pynn [1] used the Ornstein-Zernike (O-Z) equation to describe polar fluids in a very strong field. There are some problems associated with using the O-Z equation for such a system that are not adequately resolved by [1].

de Gennes and Pincus [2] have noted that for a system of dipoles in an external field, the second virial coefficient must be dependent on the shape of the total volume. In an isotropic system, the fluid is not aligned and such a system cannot exhibit sample shape dependent properties. However, if a field is applied, certain properties depend on the shape of the system as a result of the long-ranged nature of the dipole - dipole interaction. Such sample dependence was not included in the work of [1]. In section 5.3, an ideal gas of dipolar particles is used to investigate shape - dependence.

In [1], the field is considered to be so strong that the dipoles are totally aligned. For this, the O-Z equation takes a particularly simple form. It does not, however, allow the effects of field strength to be studied. To do this, movement of the dipole axis with

respect to external field must be included in the model. The theory of Chapter 2 should, in principle, describe the effects due to external fields of all strengths. It is only in the limit of very weak fields, and very strong fields, that these equations degenerate into simple forms. The former is useful for modelling electrostriction and the latter for induced coagulation. Attention will be directed to the latter case. As an example, the so-called 'ferro-fluid' is introduced in section 5.2.

## 5.2 Ferrofluids

Ferrofluids are colloidal dispersions of ferromagnetic grains. The grains are roughly spherical particles with radii  $> 100 \text{ \AA}$  and coated with a surfactant (e.g. oleic acid) to keep the system dispersed. The permanent magnetic moment is large ( $\beta\mu^2/a^3 \dagger \approx 0(10)$ ) and so in a strong external magnetic field, the grains combine to form chains that repel each other.

For fluids with a small concentration of colloidal particles, linear chains of up to 10 particles are expected. The chains are constantly breaking up and reforming under the action of thermal agitation. As the number density of the ferromagnetic particles increases and the chains become longer, they could easily deform into more complicated structures [1,2,14]. If the overall interaction between the two particles becomes too attractive, they will coagulate to form large agglomerates, the sizes of which are determined by

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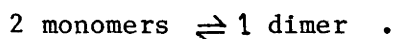
<sup>†</sup> Here,  $\mu$  is the permanent dipole moment,  $a$  the diameter of the particle and  $\beta = 1/kT$ .

mechanical shears, rather than thermal motion [4,5].

The ability to coagulate and <sup>\*</sup>disperse ferromagnetic materials by merely increasing or decreasing an external magnetic field has applications [7,8] in laboratory and medical work as well as flocculation of minerals [6].

For most ferrofluids, van der Waals attractions are expected to be negligible compared to magnetic attractions. The ferromagnetic grains can be considered to be hard spheres with permanent magnetic dipoles. If the external field  $H$  is strong enough the field fluctuations caused by the presence of other particles become insignificant and so the effective dipole moment (permanent + induced) remains relatively constant.

The principal theory describing agglomeration is due to Jordan [13]. Jordan treats chain formation by analogy to polymerisation and chemical reaction. With this analogy Jordan calculates the dissociation energy for the reaction



Given that the parameters of the system all are such that only chains of 1 or 2 particles can exist, then, by using the dissociation energy, one can calculate the number of each type of chain.

This notion is extended to longer chains after making certain assumptions

- (i) The chains remain simple linear chains
- (ii) There are no chain-chain interactions

(iii) Dipole-dipole interactions are limited to nearest neighbours and next nearest neighbours. Experiments [7-12] generally show more agglomeration than predicted by Jordan's theory.

In principle, the techniques of Liquid State Physics can be applied to the system without the aforementioned assumptions. This is discussed in section 5.4.

### 5.3 Shape Dependence

The dependence of macroscopic properties on the shape of the sample is best illustrated by an ideal gas of totally aligned dipoles. If the shape of the system is either a sphere or a rectangular prism its electrostatic properties are equivalent to the systems shown in Fig. 5.1.

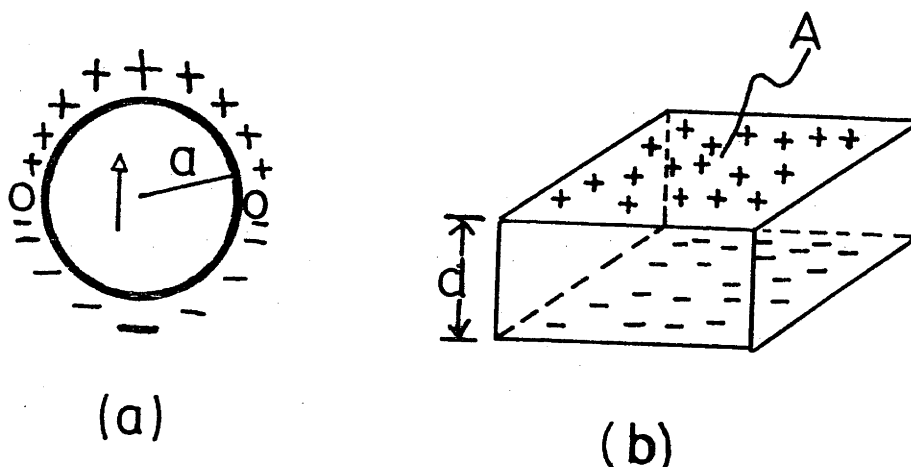


Fig. 5.1 Sphere (a) and Prism (b) with surface charge. For the sphere the charge is proportional to  $\cos\theta$  where  $\theta$  is the angle as measured for the dipole axis. For the prism the charge distribution is uniform.

The electrostatic properties of these systems can be treated exactly. For example, in Appendix 1, the free energy of the two systems of aligned dipoles are

$$F_o = \frac{2\pi\rho}{3} \mu^2 V \quad (\text{sphere}) \quad (5.1a)$$

$$V = \frac{4\pi}{3} \rho a^3 \quad (5.1b)$$

$$F = 2\pi \rho \mu^2 V \quad (\text{prism}) \quad V = Ad \quad (5.2)$$

where  $a$  is the radius of the sphere,  $\rho$  the density,  $\mu$  the dipole moment,  $A$  the area of the top surface of the prism and  $d$  the depth of the prism.

Thus the free energy depends on the shape of the sample. One may ask what this implies about the pressure and compressibility. For example, it is not clear whether the expressions for the pressure and compressibility as obtained by differentiating these expressions for the free energy are the same as those obtained from the virial and compressibility equations. Nor is it obvious that the stress tensor is homogeneous or isotropic. To highlight these issues, the rectangular prism-shaped sample of an ideal gas of total aligned dipoles will be used.

To investigate the pressure we will consider a prism sample to put under the stresses depicted in Fig. 5.2. The pressures  $p_1$  and  $p_2$  are chosen so that the system remains in equilibrium.

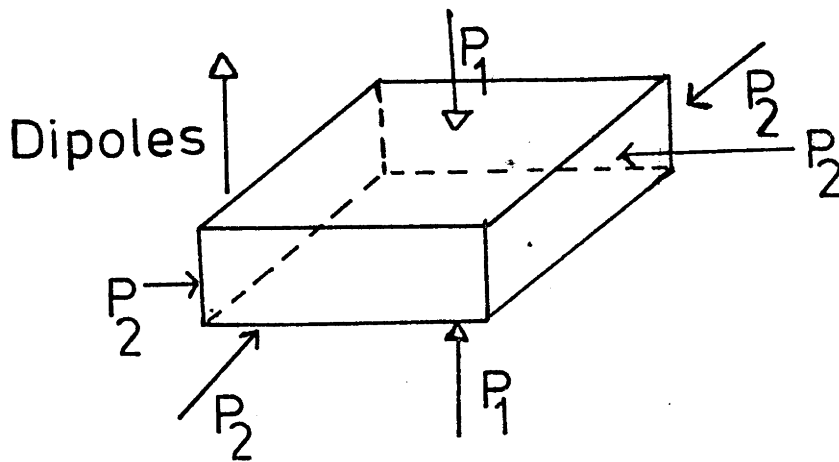


Fig. 5.2 Stresses applied normally to surface of prism as shown.

For a system of particles interacting via a short-ranged spherically symmetric potential or an isotropic system of dipolar particles

$$P_1 = P_2 (= p, \text{ say}) \quad (5.3)$$

and the stress tensor  $\underline{\underline{\sigma}}$  at any point in the sample is given by

$$\underline{\underline{\sigma}} = -p \underline{\underline{I}} \quad (5.4)$$

It is not clear whether this is the case with the aligned dipolar fluid. For the described prism system, the stress tensor can be determined at all points in the body by calculating the force one part of the body exerts on the other across a plane. It is found (Appendix 1) that

$$\underline{g} = - p \underline{I} \quad (5.5)$$

where

$$P_1 = P_2 = p = - \left( \frac{\partial F}{\partial V} \right)_N \quad (5.6)$$

Thus for this simple system, the two methods of calculating the pressure are consistent. Is the same true for compressibility?

The compressibility for this system is given by (Appendix 1)

$$K = \left( \frac{\partial p}{\partial V} \right)_T = - \frac{NkT}{V^2} \left( 1 + \frac{8\pi\beta}{3} \frac{N}{V} \mu^2 + \dots \right) \quad (5.7)$$

This agrees with that calculated from the compressibility equation

$$K\rho kT = 1 + \rho \int_V h(\underline{r}) d\underline{r} \quad (5.8)$$

It is worth noting that the integral in the compressibility equation is only conditionally convergent and hence shape dependent. Because of the conditional convergence the derivation of (5.8) needs to be modified.

Another result of the shape dependence is the problem of relating the integral in equation (5.8) to a Fourier transform. It is only for a spherical shaped system that one can use the transform (2.61) (provided such transforms are well defined) and only for this system can one equate the integral (5.8) to the transform

$$\int h(\underline{r}) d\underline{r} = \tilde{h}_{00}^{000}(0) \quad (5.9)$$

where  $\tilde{h}_{00}^{000}(k)$  is defined in (2.44).

Thus for the ideal gas of totally aligned dipoles the various expressions for the pressure are consistent. While the results for a general system are unknown, the simple example given here illustrates some of the problems associated with shape dependence.

#### 5.4 Totally Aligned Particles

In Chapter 2, it was shown that the correlation function  $f(f = g, h, c)$  of a system of totally aligned dipoles can be written as

$$f(1,2) = \sum_{\substack{mn\ell \\ \mu\nu}} f_{\mu\nu}^{mn\ell}(r) \psi_{\mu\nu}^{mn\ell}(\omega_1, \omega_2, \hat{\underline{r}}, \hat{\underline{z}}) \quad (5.10)$$

where  $\omega_1$  is the orientation of molecule 1,  $\hat{\underline{r}}$  the orientation of the intermolecular axis,  $\hat{\underline{z}}$  a frame in which the z-axis is parallel to  $\underline{E}$ ,  $r$  is the intermolecular separation. In the limit of the angles  $\theta_1, \theta_2$  (see. Fig. 5.3) going to zero, the functions

$$\psi_{\mu\nu}^{mn\ell} \rightarrow \delta_{\mu,0} \delta_{\nu,0} P_{\ell}(\cos\theta) \quad , \quad (5.11)$$

and the expansion (5.11) degenerates to

$$f = \sum_f f_{\ell}(r) P_{\ell}(\cos\theta) \quad , \quad (5.12)$$



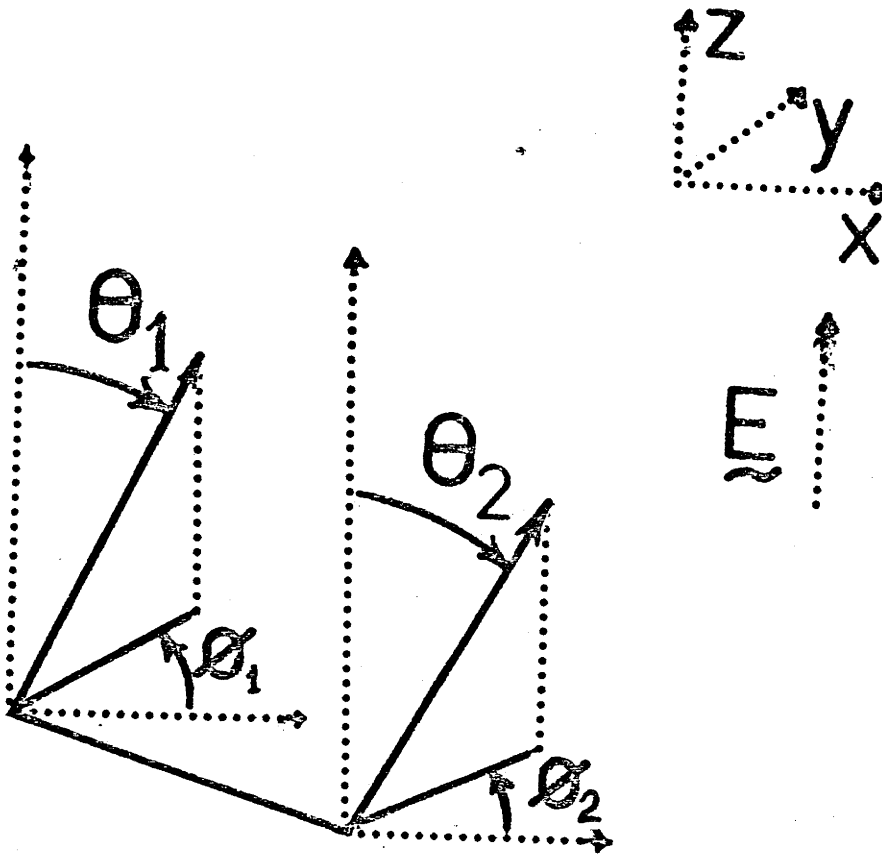


Fig. 5.3 Two dipoles in an external field  $E$ .

where

$$f_{\ell}(r) = \sum_{m,n} f_{\mu\nu}^{mn\ell}(r) \quad . \quad (5.13)$$

The angles  $\theta_1, \theta_2$  going to zero is equivalent to the orientational distribution function  $\rho(\theta)$  approaching a delta function

$$\text{i.e.} \quad \rho(\theta) = \frac{\rho_0}{2\pi} \delta(\theta) \quad (5.14)$$

where  $\rho_0$  is the density of the isotropic system. In this limit the

O-Z equation approaches (2.60)

$$\tilde{h}_\ell(k) = \tilde{c}_\ell(k) + \sum_{\ell', \ell''} \rho_0 \tilde{c}_{\ell'}(k) \tilde{h}_{\ell''}(k) \begin{pmatrix} \ell & \ell' & \ell'' \\ 0 & 0 & 0 \end{pmatrix}^2 (2\ell + 1) \quad (5.15)$$

where

$$\tilde{h}_\ell(k) = 4\pi i^\ell \int_0^\infty dr r^2 j_\ell(kr) h_{\mu\nu}^{mn\ell}(r) \quad (5.16)$$

and

$$\begin{pmatrix} m & n & \ell \\ \mu & \nu & \lambda \end{pmatrix}$$

is a Wigner 3-J symbol (Appendix 3 of Chapter 2). Equations (5.13), (5.14) - (5.16) were obtained in [1].

In [1] the series (5.13) was truncated at  $\ell = 2$ . Such a scheme would be appropriate for a system containing a concentrated dispersion. For this system, the steric effects become dominant and the distribution of particles about any given particle is spherically symmetrical. For low concentrations, the dipolar interactions become dominant and chaining occurs. The choice of  $\ell = 0, 2$  would be inadequate to describe chaining. Another choice of  $\ell$  will be discussed later.

In [1], the equations, obtained from discarding all terms for which  $\ell > 2$  in the invariant expansion, were solved using the MSA closure. They found that the  $\lim_{k \rightarrow 0} h_2(k)$  did not approach zero. It was claimed that this 'implies an unphysical angular behaviour'

for the structure factor. To overcome this, Hayter and Pynn developed a scheme in which  $h_2(k)$  was forced to zero.

It was explained in section 5.3 that the Fourier transform of the indirect correlation function is conditionally convergent and for this reason

$$\lim_{k \rightarrow 0} h_2(k) \neq 0$$

Thus this scheme has no physical basis. Moreover, this scheme is unnecessary. Such modifications have little influence on the correlation functions for separations of less than four diameters. This is the range which interests us.

The results of [1] seem to suggest chaining. The correlation functions  $g_{||}(r)$  and  $g_{\perp}(r)$  are shown in Fig. 5. The function  $g_{||}(r)$  is the correlation function of particles parallel to the field and is  $g_{\perp}(r)$  the correlation function of those perpendicular to the field. the function  $g_{||}(r)$  is more structured than  $g_{\perp}(r)$ . This is what would be expected if chaining occurs.

### 5.5 Imperfect alignment

Perfect alignment only occurs for infinite fields. Normally there is some favourable range of orientations of the axes of the dipoles with respect to the fields. By allowing this in the model, one can incorporate the effects of field strength and its effect on agglomeration. However one must know the relationship between angular density distribution  $\rho(\theta)$  with field strength  $E$  and the

correlations of the other particles. This may be obtained either theoretically or from experimental data.

The term  $\rho(\theta)$  is even in the angle  $\theta$  and so for small  $\theta$ , can be written

$$\rho(\theta) = \frac{\rho_0}{2\pi} \delta(\cos\theta - 1) + \rho_1 \delta'(\cos\theta - 1) \quad (5.17)$$

where  $\rho_0, \rho_1$  depend on field strength. In the limit of infinite field strength  $\rho_1$  is zero and  $\rho_0$  becomes the bulk density. Our interest at this stage is not the calculation of  $\rho_0, \rho_1$  but rather the inclusion of a density of the form (5.17) into the O-Z equation. The equation (5.16) relies on the angle  $\theta$  in Fig. 5.3 being small whereas  $\phi$  takes any value. In this limit the cylindrical invariants

$\psi_{\mu\nu}^{mn\ell}$  as defined in Chapter 2 asymptote as follows

$$\psi_{00}^{mn\ell} = \left\{ 1 - \frac{(m(m+1)\theta_1^2 + n(n+1)\theta_2^2)}{4} \right\} P_\ell(\hat{R}) + O(\theta^4) \quad (5.18)$$

$$\psi_{0\pm 1}^{mn\ell} = \left\{ \frac{\sqrt{n(n+1)}\theta_2 e^{\pm i\phi_2}}{2} \right\} D_{0\pm 1}^\ell(\hat{R}) + O(\theta^3) \quad (5.19)$$

$$\psi_{0\pm 2}^{mn\ell} = \left\{ \frac{\sqrt{(n-1)n(n+1)(n+2)}}{8} \theta_2^2 e^{\pm i2\phi} \right\} D_{0\pm 2}^\ell(\hat{R}) + O(\theta^4) \quad (5.20)$$

$$\psi_{11}^{mn\ell} = \left\{ \frac{\sqrt{m(m+1)n(n+1)}}{4} \theta_1\theta_2 e^{i(\phi_2 - \phi_1)} \right\} D_{00}^\ell(\hat{R}) + O(\theta^4) \quad (5.21)$$

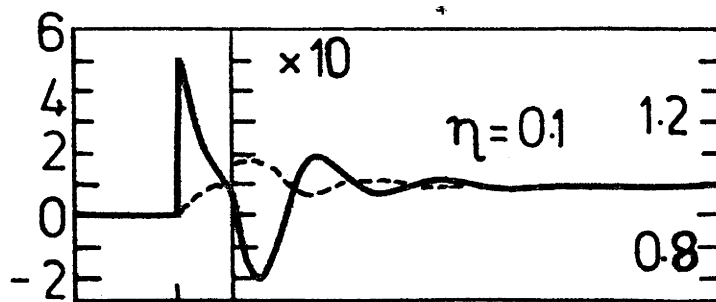


Fig. 5.4 The correlation functions  $g_{\parallel}$  (—) and  $g_{\perp}$  (---) for totally aligned dipolar fluid.

$$\psi_{1-1}^{mn\ell} = - \left\{ \frac{\sqrt{m(m+1)n(n+1)}}{4} \theta_1 \theta_2 e^{i(\phi_1 + \phi_2)} \right\} D_{0-2}^{\ell}(\hat{R}) + O(\theta^4) \quad (5.22)$$

The calculation of the indirect correlation function

$$h(1,2) = \sum_{\substack{mn\ell \\ \mu\nu}} h_{\mu\nu}^{mn\ell}(r) \psi_{\mu\nu}^{mn\ell}(1,2,\hat{R},\hat{E})$$

to order  $\theta^2$  requires a knowledge of the following quantities

$$(i) \quad h_0^{\ell}(r) = \sum_{m,n} h_{00}^{mn\ell}(r) \quad (5.23)$$

$$(ii) \quad h_1^{\ell}(r) = \sum_{m,n} n(n+1) h_{00}^{mn\ell}(r) \quad (5.24)$$

$$(iii) \quad h_2^{\ell}(r) = \sum_{m,n} \sqrt{n(n+1)} \quad h_{01}^{mn\ell}(r) \quad (5.25)$$

$$(iv) \quad h_3^{\ell}(r) = \sum_{m,n} \frac{\sqrt{m(m+1)n(n+1)}}{2} \quad h_{11}^{mn\ell}(r) \quad (5.26)$$

$$(v) \quad h_4^{\ell}(r) = \sum_{m,n} \sqrt{n(n+1)(n+2)(n-1)} \quad h_{02}^{mn\ell}(r) \quad (5.27)$$

$$(vi) \quad h_5^{\ell}(r) = \sum_{m,n} \frac{\sqrt{m(m+1)n(n+1)}}{2} \quad h_{1-1}^{mn\ell}(r) \quad . \quad (5.28)$$

These quantities must come from the O-Z equation. The term

$\delta'(\cos\theta - 1)$  is not difficult to use. Integration by parts can be used in the angular intergration to give

$$\int \delta'(\omega_3) D_{o\lambda_1}^m(\omega_3) D_{o\lambda_2}^n(\omega_3) d\omega_3$$

$$= - \frac{\partial}{\partial \cos \theta_3} (D_{o\lambda_1}^m(\omega_3) D_{o\lambda_2}^n(\omega_3)) \Big|_{\theta_3=0; \lambda_1+\lambda_2=0}$$

$$= \left\{ - \delta_{\lambda_1, \lambda_2, 0} \frac{\partial D_{oo}^n}{\partial (\cos \theta_3)} (\phi, 0, \partial) - \delta_{\lambda_2, 0} \frac{\partial D_{o\pm 1}^m}{\partial (\cos \theta_3)} (\phi, 0, \gamma) \right\} .$$

Using the relation

$$\frac{\partial D_{oo}^n}{\partial \cos \theta_3} (\phi, 0, \gamma) = \frac{m(m+1)}{2} \quad (5.29)$$

the O-Z equation becomes

$$\tilde{h}_{\mu\nu}^{mn\ell}(k) = \tilde{c}_{\mu\nu}^{mn\ell}(k) + \sum_{\ell', \ell'', m', m''} \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & \ell'' & \ell \\ \mu & -\nu & -\lambda \end{pmatrix} (2\ell+1)(-)^{\lambda}$$

$$\tilde{c}_{\mu 0}^{mn' \ell'}(k) \tilde{h}_{0\nu}^{m' n \ell''}(k)$$

$$\times \left\{ \rho_0 - \rho_1 \left( \frac{n'(n'+1)}{2} + \frac{m'(m'+1)}{2} \right) \right\}. \quad (5.30)$$

For  $\mu = \nu = 0$

$$\tilde{h}_{00}^{mn\ell}(k) = \tilde{c}_{00}^{mn\ell}(k) + \sum \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 (2\ell+1) \tilde{c}_{00}^{mn' \ell'}(k) \quad (5.31)$$

$$\tilde{h}_{00}^{m' n \ell''}(k) \left\{ \rho_0 - \rho_1 \left( \frac{n'(n'+1)}{2} + \frac{m'(m'+1)}{2} \right) \right\}.$$

Summation over  $m, n$  implies

$$(i) \quad \tilde{h}_0^{\ell}(k) = \tilde{c}_0^{\ell}(k) + \sum \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 (2\ell+1) \quad (5.32)$$

$$\times \left\{ \rho_0 \tilde{c}_0^{\ell'}(k) \tilde{h}_0^{\ell''}(k) - \rho_1 \tilde{c}_1^{\ell'}(k) \tilde{h}_1^{\ell''}(k)(-)^{\ell''} \right\}$$

$$(ii) \quad \tilde{h}_1^{\ell}(k) = \tilde{c}_1^{\ell}(k) + \sum \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 (2\ell+1) \rho_0 (-)^{\ell''} \quad (5.33)$$

$$\times \tilde{c}_0^{\ell'}(k) \tilde{h}_1^{\ell''}(k).$$

(5.32) and (5.33) can be solved together with a closure to give

$h_0^\ell(r)$  and  $h_1^\ell(r)$ . For  $\mu = 0$ ,  $\nu = 1$  the O-Z equation becomes

$$\begin{aligned} \tilde{h}_{01}^{mn\ell}(k) &= \tilde{c}_{01}^{mn\ell}(k) - \sum \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & -1 & 1 \end{pmatrix} (2\ell+1) \\ &\times \tilde{c}_{00}^{mn'\ell'}(k) \tilde{h}_{01}^{m'n\ell''}(k) \rho_0 \end{aligned} \quad (5.34)$$

and so

$$\tilde{h}_2^\ell = \tilde{c}_2^\ell - \sum \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & -1 & 1 \end{pmatrix} (2\ell+1) \tilde{c}_0^{\ell'} \tilde{h}_2^{\ell''}. \quad (5.35)$$

Thus if  $\tilde{h}_0^\ell(k)$  and  $\tilde{c}_0^\ell(k)$  have been calculated, (5.35) can be solved together with a closure. Equations for the other quantities can be similarly calculated to give

$$\tilde{h}_3^\ell = \tilde{c}_3^\ell + \sum \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & \ell'' & \ell \\ 1 & -1 & 0 \end{pmatrix} (2\ell+1) \tilde{c}_2^{\ell'} \tilde{h}_2^{\ell''} \rho_0 (-)^{\ell'+1} \quad (5.36)$$

$$\tilde{h}_4^\ell = \tilde{c}_5^\ell + \sum \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 2 & -2 \end{pmatrix} (2\ell+1) \tilde{c}_0^{\ell'} \tilde{h}_5^{\ell''} \rho_0 \quad (5.37)$$

$$\tilde{h}_5^\ell = \tilde{c}_5^\ell + \sum \begin{pmatrix} \ell' & \ell'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & \ell'' & \ell \\ 1 & 1 & -2 \end{pmatrix} (2\ell+1) (-)^{\ell'+1} \tilde{c}_2^{\ell'} \tilde{h}_2^{\ell''} \rho_0. \quad (5.38)$$

Apart from (5.32) and (5.33) there is no coupling between the quantities  $\tilde{h}_j^\ell$  and so the equations (5.34 - 5.38) can be solved one by one. There are also many similarities between the equations, so



special treatment is not required for the various equations. Therefore despite the proliferation of equations the system is not much more difficult to solve than the original case with the totally aligned dipoles.

## 5.6 Discussion

The main aim of this chapter has been to write the O-Z equation in a useful form for cylindrically symmetric systems. This is possible in the limits of very weak and very strong fields. The O-Z equation in the latter limit has particular relevance to the agglomeration of ferro-fluids [1]. The equations to do this have been developed in section 5.5.

A discussion of ferro-fluids necessitates a discussion of aligned dipoles which in turn necessitates an understanding of shape dependence of the sample. Such shape dependence is not understood properly and some work needs to be done to resolve a number of issues. In section 5.3, the simple case of an ideal gas was discussed as an example to highlight these issues.

The work of [1] suggests chaining but whether the results are quantitatively better than can be produced by physical intuition is questionable. There are many reasons for this.

: The MSA closure is not expected to be very accurate (as shown in the isotropic case).

: The actual process of chaining itself suggests a process in which the distribution of inter-grain axes is anything but spherical. Under these circumstances it is expected that the consideration of only 2 harmonics would be inaccurate.

Perhaps an expansion similar to the  $\delta, \delta'$ .. expansion described in the later sections would yield some interesting results on the extent of chaining. This may be more appropriate at lower densities.

: The imperfect alignment of particles could have a large influence on correlation functions.

Nevertheless the model of [1] is useful in that because the particles are nearly aligned it is possible without being overburdened with computer work to calculate correlation functions for this system. Relating this system with the work in Chapter 2 on cylindrically symmetric systems allows effects such as non-alignment of particles to be included in the model. Once problems such as shape dependence are resolved (and these are not trivial) there is a wealth of interesting properties to investigate.

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### Appendix 5.1

Consider a rectangular prism shaped sample containing an ideal gas of hard spheres imbedded with very weak dipoles. Since we are dealing with an ideal gas, we assume

$$\begin{aligned} g(r) &= 0 && \text{if } r < R \\ &= 1 && \text{if } r > R \end{aligned} \quad (\text{A.1})$$

where  $R$  is the hard sphere diameter. Using (A.1) in the equation for the internal energy,  $U$  gives

$$U = \frac{1}{2} \rho^2 \int d\mathbf{l} \int d\mathbf{2} g(1,2) u(1,2) \quad (\text{A.2})$$

$$= -\frac{1}{2} \rho^2 \int d\mathbf{l} \hat{\underline{\mu}}_1 \cdot \int_{|\underline{\mathbf{r}}_1 - \underline{\mathbf{r}}_2| > R} d\mathbf{2} \underline{\tilde{E}}(1,2) \quad (\text{A.3})$$

where  $\underline{\tilde{E}}(1,2)$  is the electric field at 1 due to the dipole at 2. The integral

$$\rho \int_{|\underline{\mathbf{r}}_1 - \underline{\mathbf{r}}_2| > R} d\underline{\mathbf{r}} \cdot \underline{\tilde{E}}(1,2) = \rho \int_S d\underline{\mathbf{S}} \cdot \underline{\mathbf{E}}(1,2) = -\frac{8\pi\mu\rho}{3} \quad (\text{A.4})$$

Here  $S$  is the surface shown in Fig. A.1. The sphere is centred at position 1 and the prism is considered large enough that edge effects

can be ignored. In the approximation of an ideal gas of totally

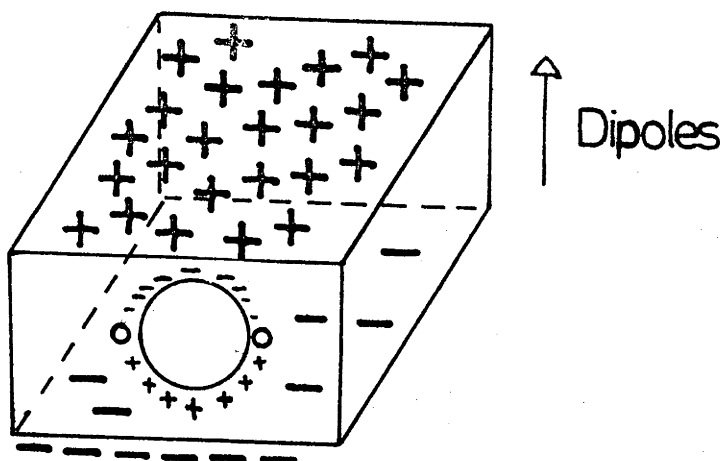


Fig. A.1

aligned dipoles, the energy is the same as the free energy and equals

$$U = F = \frac{4\pi}{3} \frac{N^2 \mu^2}{V} \quad (\text{A.5})$$

Here  $N$  is the number of dipoles in the sample, and  $V$  is the volume of the sample. One expression for the pressure  $P$  is given by

$$P_1 = - \frac{\partial F}{\partial V} = - \frac{4\pi}{3} \frac{N^2 \mu^2}{V^2} \quad (\text{A.6})$$

now, suppose the prism is divided into two smaller bodies as shown in Fig. A.2. There is now a possibility of part of a sphere being in one prism while its centre is in another as shown in Fig. A.3. The electrostatics of that system is equivalent to that shown in Fig. A.4. The pressure can be calculated by first determining the potential at a height  $z$  above the plane, and then determining the

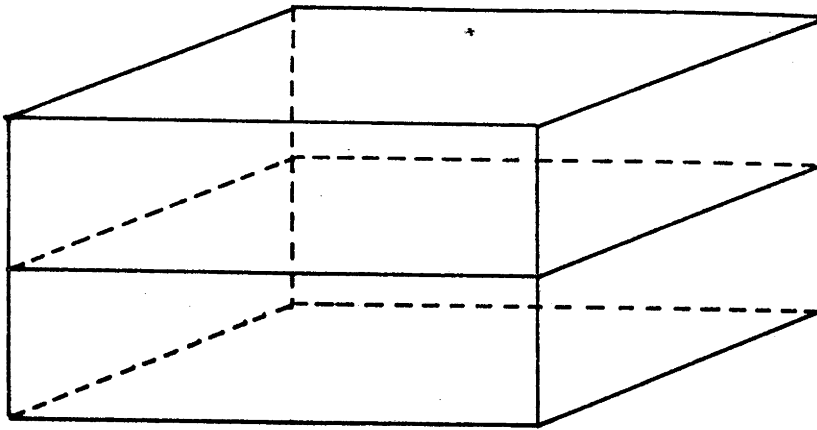


Fig. A.2

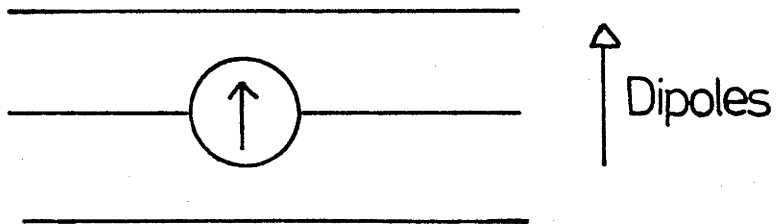


Fig. A.3

electrostatic force on the body. This gives

$$P_1 = \frac{4\pi}{3} \rho^2 \mu^2. \quad (\text{A.7})$$

This agrees with (A.5) and (A.6). The term  $p_2$  (see Fig. 5.2) can be calculated in a similar manner by splitting the prisim as in Fig.

A.5. It is found that

$$P_2 = p_1 = p.$$

The inverse compressibility is

$$\left(\frac{\partial P}{\partial V}\right)_{N,T} = -\frac{NkT}{V^2} \left(1 + \frac{8\pi\beta}{3} \frac{N}{V} \mu^2 + \dots\right) \quad (\text{A.8})$$

where the ideal gas term is included. The term

$$1 + \rho \int h(\underline{r}) d\underline{r}$$

is equal to

$$1 - \frac{4\pi}{3} \rho(2R)^3 - \frac{2\beta}{\rho V} \left(\frac{4\pi}{3} \rho^2 \mu^2 V\right) \quad (\text{A.9})$$

Thus

$$\begin{aligned} -\frac{\rho kT}{V(1 + \rho \int h(\underline{r}) d\underline{r})} &= \frac{NkT}{V^2} \left(1 + \frac{8\pi\beta}{3} \frac{N}{V} \mu^2 + \dots\right) \\ &= \left(\frac{\partial P}{\partial V}\right)_{N,T}. \end{aligned} \quad (\text{A.10})$$

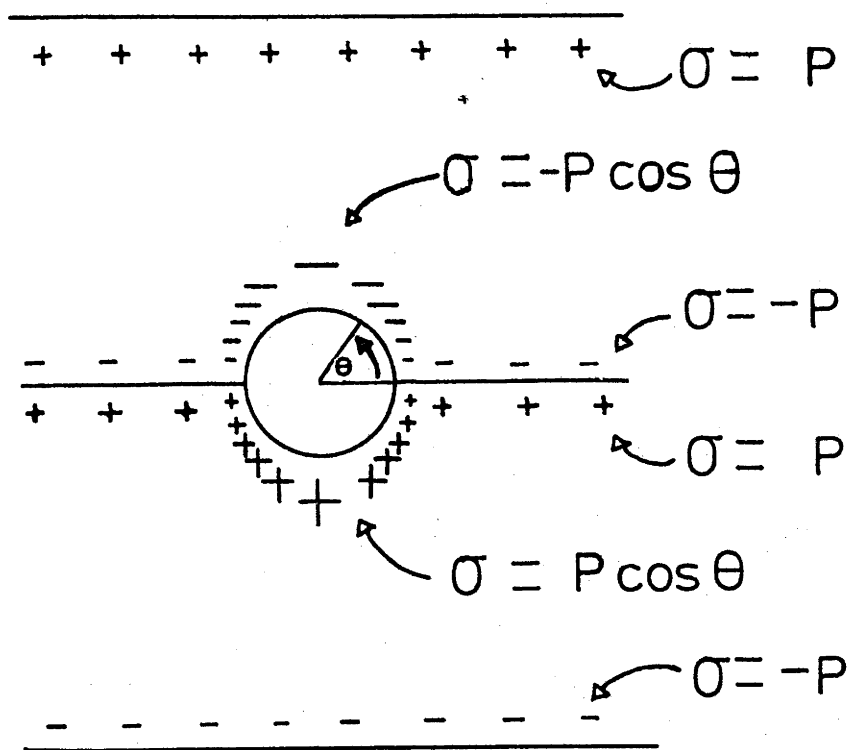


Fig. A.4

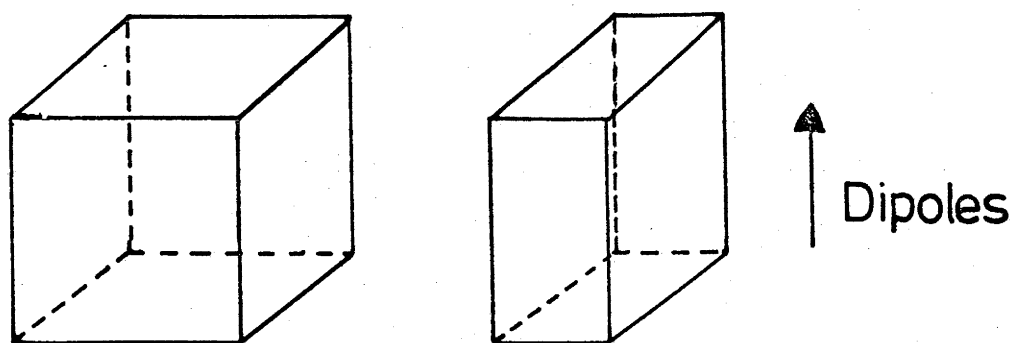


Fig. A.5



## CHAPTER 6

## FLUIDS IN AN EXTERNAL FIELD

6.1 Introduction

Over the last two decades, much work has been directed towards studying the effect of an external field on a fluid. Not only does this study have the obvious applications, such as studying a system of dipoles in an external field, but has less obvious applications such as studying phase transitions and surfaces. It is this second class of applications that will be used in the work on liquid crystals. Because the techniques developed for external potentials are essential for the work in Chapter 7, this chapter is devoted to a discussion of these techniques.

First, a set of integro-differential equations describing the effect of an external field on the density distribution is derived from the definition of the grand potential. The free energy of such a change is also calculated.

Next, the behaviour of fluids near a surface is described in terms of an external potential. In particular, a scheme is developed for calculating the free energy of a fluid between 2 surfaces. This is done in the Landau Approximation. The surface forces are treated as being very short-ranged. An immediate application is the electrical double layer. It is shown that even a crude approximation

for the direct correlation function yields the well-known Poisson-Boltzmann equation and the Verwey-Overbeek expressions for the free energy.

## 6.2 Integro-Differential Equations

The equilibrium density distribution of a fluid under the influence of an applied external field  $V_{\text{ext}}$  can be calculated in a number of ways. A class of methods involves integro-differential equations. Six examples are given here. These equations are obtained by differentiating the grand potential  $\Omega$  where  $\Omega$  is defined by

$$e^{-\beta\Omega} \equiv \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N! h^{3N}} \int d\mathbf{l} \dots d\mathbf{N} \int dp_1 \dots dp_N e^{-\beta H_N} (d\mathbf{l} = d\mathbf{r} d\omega) \quad (6.1)$$

and the density distribution

$$\rho(\mathbf{l}) \equiv e^{\beta\Omega} \sum_{N=1}^{\infty} \frac{e^{\beta\mu N}}{(N-1)! h^{3N}} \int d\mathbf{2} \dots d\mathbf{N} \int dp_1 \dots dp_N e^{-\beta H_N} \quad (6.2)$$

with respect to some parameter. Here

$$H_N = H_0 + \sum_{i=1}^N V_{\text{ext}}(\mathbf{l}_i) \quad (6.3)$$

where  $H_0$  is the zero-field Hamiltonian and  $i=1, \dots, N$  are the positions and orientations of the particles.

The best known example, the BGY equation, is obtained by differentiating equation (6.2) w.r.t. the position

$$\underline{\nabla} \rho(1) = - \beta \rho(1) \underline{\nabla} V_{\text{ext}}(1) + \beta \int d2 \underline{\nabla} u(1,2) \rho(1,2) \quad (6.4)$$

or

$$\underline{\nabla} \ln \rho(1) = - \beta \underline{\nabla} V_{\text{ext}}(1) + \beta \int d2 \underline{\nabla} u(1,2) \overset{\rho(2)}{\cancel{\rho(1,2)}} g(1,2) \quad . \quad (6.5)$$

A similar equation [1] is obtained by differentiating <sup>equation</sup> (6.2) w.r.t. the orientation  $\omega_1$

$$\underline{\nabla}_{\omega_1} \ln \rho(1) = - \beta \underline{\nabla}_{\omega} V_{\text{ext}}(1) - \beta \int d2 \underline{\nabla}_{\omega} u(1,2) \rho(2) g(1,2) \quad . \quad (6.6)$$

Here  $g(1,2)$  is the pair correlation function. A third equation is obtained by considering the effects of translating the origin of the external field. Since the density distribution depends explicitly on the field, such a translation in the external potential will result in a similar translation in the density distribution. Thus, if the external field is translated an infinitesimal distance  $\delta \underline{x}$ , the new density distribution  $\sigma(x)$  resulting from the new field  $w(x)$  is

$$\sigma(1) = \rho(1 + \delta \underline{x}) = \rho(1) + \underline{\nabla} \rho(1) \delta \underline{x} \quad . \quad (6.7)$$

Using

$$w(1) = V(1 + \delta \tilde{x}) \approx V(1) + \underline{V} V(1) \delta \tilde{x} \quad , \quad (6.8)$$

it is shown in Appendix 1 that

$$\underline{V} \ln \rho(1) = - \beta \underline{V} V_{\text{ext}}(1) + \int d2 \, c(1,2) \underline{V} \rho(2) \quad (6.9)$$

where  $c(1,2)$  is the direct correlation function.

A similar equation [1] is obtained by considering the effects of infinitesimal rotation  $\delta \tilde{\omega}$ .

Consider a process in which the external field is applied slowly enough for equilibrium to be maintained throughout the process.

Mathematically this can be analysed by writing the Hamiltonian as

$$H_N = H_0 + \lambda \sum_{i=1}^N V_{\text{ext}}(i) \quad (6.10)$$

where  $\lambda$  runs from 0 to 1. It is found (Appendix 2) that

$$\frac{\partial \ln \rho_\lambda(1)}{\partial \lambda} = - \beta V_{\text{ext}}(1) + \int d2 \, c_\lambda(1,2) \frac{\partial \rho_\lambda(2)}{\partial \lambda} \quad (6.11)$$

where the subscripts  $\lambda$  indicate the quantities at the stage  $\lambda$  of the process.

A more useful approach is to apply the external field in such a way that the equilibrium density follows the path

$$\rho_\alpha(1) = \rho_0 + \alpha(\rho(1) - \rho_0) \quad (6.12)$$

where  $\rho(1)$  is the final equilibrium density and  $\alpha$  runs from 0 to 1. To do this,  $\lambda$  must be a function of position and  $\alpha$ , i.e.

$$H_N = H_0 + \sum_{i=1}^N V_{\text{ext}}(i) \lambda(i, \alpha) \quad . \quad (6.13)$$

In Appendix 3 it is shown that

$$\ln\left(\frac{\rho(1)}{\rho_0}\right) = -\beta V_{\text{ext}}(1) + \int_0^1 d\alpha \int d2 c_\alpha(1,2) [\rho(2) - \rho_0] \quad . \quad (6.14)$$

All of these equations have a similar form. The LHS of (6.4) and (6.7), for example, is the mean force on particle 1. This is written as the sum of the direct influence of the field  $-\beta \nabla V_{\text{ext}}(1)$  plus the indirect effect through the other particles. These integro-differential equations are the basis of the free energy calculations in the next section.

### 6.3 Free Energy

To be able to calculate certain forces and interfacial energies it is necessary to know the free energy. However the calculation of the free energy has taken on an even more important role since it is often more convenient to minimise the free energy to obtain the equilibrium density than to solve the integro-differential equations. This has led to a number of minimisation schemes [6-12].

Before any calculations are done it is necessary to distinguish between two different definitions of the change in free energy, or equivalently two different reference states. The first expression

$\Delta'\Omega$  is the difference in free energy between a bulk liquid with no applied external field and that of an equilibrium liquid with an applied field. This can be calculated by allowing the external field to be applied slowly enough to maintain equilibrium [cf. 6-10]. This expression of the free energy is that associated with interfacial tensions.

The second expression  $\Delta\Omega$  is the difference in the free energy between a bulk liquid with an applied internal field (i.e. not at equilibrium) and the equilibrium liquid with the same applied external field. One can think of a process in which the external field is applied so quickly to the bulk liquid, that the structure of the liquid does not have time to change.  $\Delta\Omega$  then measures the change in free energy as the liquid proceeds from this state to equilibrium. This change in free energy must be negative. The change in free energy due to the sudden application of the field to the bulk liquid is

$$\Delta''\Omega = \int d\mathbf{l} V_{\text{ext}}(\mathbf{l}) \rho_0 \quad (6.15)$$

so that

$$\Delta\Omega = \Delta'\Omega - \int d\mathbf{l} V_{\text{ext}}(\mathbf{l}) \rho_0 \quad (6.16)$$

In calculating  $\Delta\Omega$ , we first calculate  $\Delta'\Omega$  as described in the previous paragraph and then subtract the term  $\Delta''\Omega$ .

Suppose the external field is gradually applied in such a way that the equilibrium density at some stage  $\alpha(\alpha \in [0,1])$  of the process is

$$\rho_{\alpha}(1) = \rho_0 + \alpha (\rho(1) - \rho_0) \quad . \quad (6.17)$$

From Appendix 3 it is shown that

$$\Delta(\beta\Omega) = \beta \int_0^1 d\alpha \int dl V_{\text{ext}}(1) \frac{\partial \lambda}{\partial \alpha}(1) \rho_{\alpha}(1) - \int \rho_0 dl \beta V_{\text{ext}}(1) \quad (6.18)$$

$$= \int dl \int_0^1 d\alpha \alpha [\rho(1) - \rho_0] \{ \int_0^1 d2 c_{\alpha}(1,2) [\rho(2) - \rho_0] - 1 \} \quad (6.19)$$

$$+ \int dl \rho_0 \ln(\rho(1)/\rho_0)$$

$$= \int dl \beta V_{\text{ext}}(1) (\rho(1) - \rho_0) + \int dl \rho(1) \ln\left(\frac{\rho(1)}{\rho_0}\right) - [\rho(1) - \rho_0] - \int dl \int_0^1 d\alpha \int_0^{\alpha} d\alpha' \quad (6.20)$$

$$c_{\alpha}(1,2) [\rho(2) - \rho_0] [\rho(1) - \rho_0] \quad .$$

Equation (6.19) is equivalent to Evan's result [6], while that of (6.22) is that of Saam and Ebner [7].

Since  $\Delta\Omega$  is always negative as the system goes from some state to the equilibrium state, a minimisation scheme could be developed to calculate the equilibrium density. Suppose the external potential is gradually applied so that equilibrium is maintained. Mathematically

this can be done with the use of an external potential  $V'(1)$  which varies from 0 to  $V_{\text{ext}}(1)$ . Suppose that when  $V'(1)$  is applied the density distribution is  $\tau(1)$ . The  $\Delta\Omega$  can be split

$$\Delta\Omega = \Delta_1\Omega + \Delta_2\Omega, \quad (6.21)$$

where

$$\begin{aligned} \Delta_1\Omega = & V_{\text{ext}}(\tau(1) - \rho_0) + \int d1 \tau(1) \ln \left( \frac{\tau(1)}{\rho_0} \right) \\ & - [\tau(1) - \tau_0] - \int d1 \int d2 \int_0^1 d\alpha \int_0^\alpha d1 c_\alpha(1,2) \\ & [\tau(2) - \rho_0] [\tau(1) - \rho_0]. \end{aligned} \quad (6.22)$$

The second term,  $\Delta_2\Omega$ , is the change in free energy in going from the state in which the density is  $\tau(1)$  to a state in which the density is  $\rho(1)$  plus the term

$$V_{\text{ext}}(\rho(1) - \tau(1))$$

From the above argument  $\Delta_2\Omega$  is negative and so

$$\Delta_1\Omega > \Delta\Omega. \quad (6.23)$$

$\Delta_1\Omega$  has the same form as  $\Delta\Omega$  but the density is  $\tau(1)$  rather than  $\rho(1)$ . Thus, one can consider  $\Delta_1\Omega$  as a function of the density with



$$\Delta\Omega_1[\tau_1] > \Delta\Omega_1[\rho_1] \quad . \quad (6.24)$$

By doing this, one can use equation (6.20) as a basis of a minimisation scheme.  $\Delta\Omega_1[\tau_1]$  is minimised by the equilibrium density and, for this density, is equal to  $\Delta\Omega$ .

The expression for the change in free energy (6.20) can be easily broken into 2 components:

$$\Delta\Omega = \Omega_{\text{ext}} + \Omega_{\text{liq}} \quad (6.25)$$

where

$$(a) \quad \Omega_{\text{ext}} = \int d\mathbf{l} \, v_{\text{ext}}(\mathbf{l}) (\rho(\mathbf{l}) - \rho_0) \quad (6.26)$$

which is the gain in free energy due to a favourable arrangement with respect to the fluid, and so

$$\Omega_{\text{ext}} < 0$$

$$(b) \quad \Omega_{\text{liq}} = \left\{ kT \int d\mathbf{l} \, \rho(\mathbf{l}) \ln \left( \frac{\rho(\mathbf{l})}{\rho_0} \right) - [\rho(\mathbf{l}) - \rho_0] \right. \quad (6.27)$$

$$\left. - \int d\mathbf{l} \int_0^1 d\alpha \int d\mathbf{2} \int_0^\alpha d\alpha' \, c_\alpha(1,2) [\rho(2) - \rho_0] [\rho(1) - \rho_0] \right\}$$

which is the free energy needed to form a density distribution  $\rho(\mathbf{l})$  and so

$$\Omega_{\text{liq}} > 0 \quad . \quad (6.28)$$

The reasoning behind this splitting is as follows. Without any external field, a bulk liquid will not spontaneously form a density distribution  $\rho(l)$ . The free energy of such distributions is greater than the bulk by an amount  $\Omega_{\text{liq}}$ . It is only the presence of an external field that makes such a distribution likely. Needless to say,

$$\Delta\Omega = \Omega_{\text{ext}} + \Omega_{\text{liq}} < 0 \quad . \quad (6.29)$$

These notions will be used later in the study of the behaviour of liquids at surfaces. The effect of the surface is to make certain arrangements of molecules favourable. The free energy associated with this effect is embodied in a term  $\Delta\Omega_s$  similar to  $\Omega_{\text{ext}}$ .

#### 6.4 Modelling Surfaces

This section describes the two most common methods of modelling the behaviour of liquids near surfaces.

The first method models the wall-liquid system as a mixture of particles of two different sizes. Suppose the diameter  $R$  of the particles of one species goes to infinity and that its density  $\rho_0$  goes to zero in such a way

$$\rho_0 R^3 \rightarrow 0 \quad .$$

Then near one of these particles, the particles of the other species will behave as near a wall. By modelling the system in this way, the techniques of equilibrium statistical mechanics can be applied to a non-uniform system.

The second model of the wall is an external potential that prevents the molecules from being in certain positions. With the single hard wall there is not only the computer simulation with which to compare numerical results but also the so-called 'contact condition' [2]. This states that the pressure the fluid exerts on the wall is the same as the pressure in bulk, and the pressure at the wall is given by  $\rho_w kT$  where  $\rho_w$  is the density at the wall. If the methods involving the Ornstein-Zernike equation are applied to the first model, the single distribution obtained does not obey the contact condition. The approximations involved with the closure of the O-Z equation allow force balance not to be obeyed.

The equations for the second model were discussed in section 6.2 and were seen to be of the form of force balance. However the correlation functions  $h(1,2)$  and  $c(1,2)$  are unknown and need to be approximated. What one would like to know is what conditions on  $c(1,2)$  and  $h(1,2)$  are needed to ensure that the contact condition holds. Carnie [4] has shown that for the BGY, equation any approximation for  $h(1,2)$  that asymptotes to the bulk expression will ensure the contact condition. To our knowledge, no such results have been derived for the other integro-differential equations.

### 6.5 Approximations for c

The need to approximate the direct correlation function  $c(1,2)$  or the indirect correlation function  $h(1,2)$  in the equations of sections 6.2 and 6.3 has led to a variety of techniques that display quite different characteristics. For example, the approximation

$$c(r) \approx \frac{1}{2\pi} \left( \tilde{c}(0) \delta(r) - \frac{\tilde{c}''(0)}{2} \delta''(r) \right) \quad (6.30)$$

for the direct correlation function of an isotropic system leads to monotonically decaying profiles. Here  $c(k)$  is the 3.D Fourier transform of  $c(r)$ . This approximation is called the Landau expansion. It is a reasonable approximation if the scale length over which there are significant changes in density is much larger than the scale length associated with the direct correlation function.

This condition is not satisfied for a fluid near a wall (see Fig. 6.1). The single distribution is similar to that shown in Fig. 6.2. Here the wavelength of the oscillations are of the order of the diameter of the particle so that the density profile has the same scale length as the direct correlation function. Obviously, what is needed is a more detailed approximation which involves the molecular nature of the correlation functions. A number of schemes [3,6-12] have used various approximations for the direct correlation function of a fluid near a wall.

The basis of the Landau expansion is that, for a density distribution that is slowly varying the free energy,  $\Omega_{liq}$  can be approximated

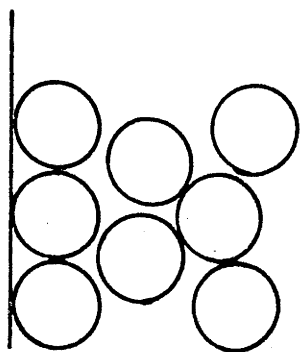


Fig. 6.1 Schematic drawing of packing of spheres against a wall.

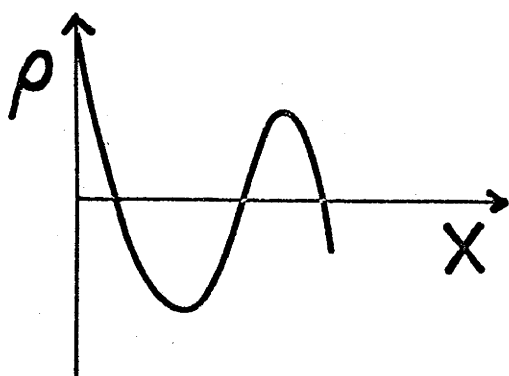


Fig. 6.2 Density distribution  $\rho(x)$  for the fluid of Fig. 6.1.

$$\Omega_{\text{liq}} \approx \int d\underline{r} \rho(\underline{r}) \Omega_0 [\rho(\underline{r})] \quad (6.31)$$

where  $\Omega_0$  is the free energy density of a bulk liquid at density  $\rho$ . One can think of each part of the liquid being connected to an infinite reservoir of fluid at density  $\rho(\underline{r})$ . However, the fluid at one place must notice that the density at a nearby place is different and this causes extra terms in the free energy expression involving derivatives of the density.

If the scale length over which there are significant changes in density is much larger than that over which such changes occur in the direct correlation function, then it can be shown (Appendix 4) that

$$\Omega_{\text{liq}} \approx \int d\underline{l} f_0(\rho(\underline{l})) + \int d\underline{l} f_2(\rho(\underline{l})) |\nabla \rho|^2 \quad (6.32)$$

where

$$f_0(\rho(\underline{l})) = \rho(\underline{l}) \ln \left( \frac{\rho(\underline{l})}{\rho_0} \right) - (\rho(\underline{l}) - \rho_0) - \frac{\tilde{c}(0)}{2} (\rho - \rho_0)^2 \quad (6.33)$$

$$f_2(\rho) = - \frac{\tilde{c}''(0)}{4} \quad (6.34)$$

where  $\tilde{c}(k)$  is the three dimensional Fourier transform of the direct correlation function. This Landau expansion is used in Chapter 7 to investigate the orientational ordering of liquid crystals at surfaces. In this, the density variation is shorter-ranged than the

orientational ordering and so at large distances from the wall, the Landau expansion can be used.

## 6.6 Electrical Double Layer

In this section a method is developed for calculating the force needed to push together 2 walls between which is a liquid. This method is restricted to those systems in which the free energy per unit area is given by

$$\frac{\Delta\Omega}{A} = \int_0^{2L} dx f(S(x), S(x)) + \Omega_S (S_w, \dot{S}_w) \quad (6.35)$$

Here  $2L$  is the separation of the walls,  $S$  is some property of the system,  $\dot{S}$  is  $\frac{dS}{dx}$ ,  $f$  the free energy density for the liquid,  $\Omega_S$  is the free energy due to the surface,  $S_w$  the value of  $S$  at the wall and  $\dot{S}_w$  is the value of  $\dot{S}$  at the wall. Consider a variation  $\delta S(x)$  in  $S(x)$ . This causes a change in free energy

$$\frac{\delta(\Delta\Omega)}{A} = \int_0^{2L} dx \delta S(x) \left( \frac{\partial f}{\partial S} - \frac{d}{dx} \left( \frac{\partial f}{\partial \dot{S}} \right) \right) \quad (6.36)$$

$$+ \delta S_w \left( \frac{\partial \Omega_S}{\partial S_w} + \frac{\partial f}{\partial \dot{S}} \Big|_w \right) + \delta \dot{S}_w \frac{\partial \Omega_S}{\partial \dot{S}_w} \quad (6.37)$$

For equilibrium ( $\delta\Omega = 0$ )

$$\frac{\partial f}{\partial S} = \frac{d}{dx} \left( \frac{\partial f}{\partial \dot{S}} \right) \quad (6.38)$$

with the boundary condition

$$\frac{\partial S_w}{\partial \dot{S}_w} = \frac{-\frac{\partial \Omega}{\partial \dot{S}_w}}{\frac{\partial \Omega}{\partial S_w} + \frac{\partial f}{\partial \dot{S}} \Big|_w} \quad (6.39)$$

If  $S_w$  is independent of  $\dot{S}_w$  then

$$\frac{\partial \Omega}{\partial \dot{S}_w} = 0 \quad (6.40)$$

If  $\dot{S}_w$  is independent of  $S_w$  then

$$\frac{\partial \Omega}{\partial S_w} = -\frac{\partial f}{\partial \dot{S}} \Big|_w \quad (6.41)$$

Before going further, a physical system with the required form (6.35) is described. It will be shown that the electrical double layer can be described using a free energy of the required form and the eqn. (6.38) corresponds to the well-known Poisson-Boltzmann equation. As will be seen, this system is excellent for illustrating the method for calculating the force between two walls.

Consider a colloid particle immersed in electrolyte. Suppose one of the ionic species preferentially adsorbs onto the surface of the colloid and creates a new surface charge. This attracts the ions of the opposite charge in the solvent. The combating effects of this attraction and entropy causes a charge distribution near the wall.

For simplicity we shall consider a 1:1 electrolyte and assume that the forces involved with adsorption at the wall are very short-



ranged so that in the solvent the external potential can be approximated by a delta function and its derivatives. A crude approximation for the direct correlation function would be

$$c_{ij}(1,2) = - \frac{\beta z_i z_j e^2}{\epsilon r_{12}} \quad (6.43)$$

where  $r_{12}$  is the separation between molecules situated at 1 and 2 and  $z_i$  is the valency of the ion of type  $i$ . Thus, only electrostatic interactions are considered and steric effects are ignored. For the ions in the solvent the integro-differential equations (6.10) and (6.14) yield the Boltzmann eqns

$$\ln \left( \frac{\rho^+(1)}{\rho} \right) = - \beta e \psi(1) \quad (6.44)$$

$$\ln \left( \frac{\rho^-(1)}{\rho} \right) = \beta e \psi(1) \quad (6.45)$$

where  $\rho^+(1)$   $\rho^-(1)$  are respectively the number densities of the cations and anions at point 1, and  $\psi(1)$  is the electrostatic potential at the same point,

$$\psi(1) = \int \frac{e'}{\epsilon r_{12}} (\rho_+(2) - \rho_-(2)) d2 \quad (6.46)$$

$$= \int d2 \frac{q(2)}{\epsilon r_{12}} + \int_s \frac{dS(2) \sigma(2)}{\epsilon r_{12}} \quad (6.47)$$

$$= \psi_1(1) + \psi_2(1) \quad . \quad (6.48)$$

The electrostatic potential consists of 2 parts, the potential

$\psi_1$  due to the charges in the solvent and the potential  $\psi_2$  due to surface charge. Here  $q(2)$  ( $\equiv \sum_i \rho_i(2) z_i e$ ) is the net charge density at a point 2 in the solvent and  $\sigma(2)$  is the net surface charge per unit area at a point 2 on the surface S of the colloid. The Poisson eqn gives

$$\begin{aligned} \nabla^2 \psi(2) &= - \frac{4\pi}{\epsilon} q(2) \\ &= + \frac{8\pi e \rho}{\epsilon} \sinh \beta e \psi(2) \quad . \end{aligned} \quad (6.49)$$

This last equation is the POISSON-BOLTZMANN equation. This can be solved provided one knows the boundary conditions (for instance the value of the surface potential or surface charge).

However, the nature of the boundary conditions comes from the term  $\Omega_{\text{ext}}$ . Since  $V_{\text{ext}}$  is very short-ranged,  $\Omega_{\text{ext}}$  should only depend on surface properties such as surface potential and surface charge. For our purposes, it is assumed that these are the only important surface properties. The exact nature of  $V_{\text{ext}}$  is unknown but some information can be gained by minimising the change in free energy. Equations (6.25) to (6.27) can be generalised for mixtures to give

$$\begin{aligned} \frac{(\beta \Delta \Omega)}{A} = & \frac{\beta \Omega_{\text{ext}}}{A} + \frac{\beta \psi_S \sigma_S}{2} + \int dl \sum_{i=\pm, -} (\rho_i(1) \ln \left( \frac{\rho_i(1)}{\rho} \right) \\ & - (\rho_i(1) - \rho) + \int dl \frac{\beta}{2} \psi(1) q(1) \end{aligned} \quad (6.50)$$

where  $A$  is the surface area of the colloid. Poisson's equation (6.46) can be used to integrate (6.50) by parts. For convenience we shall define the quantities  $\psi_+$ ,  $\psi_-$

$$\nabla^2 \psi_{\pm}(1) = \frac{4\pi}{\epsilon} e \rho_{\pm}(1) \quad (6.51)$$

$$\psi_+(1) + \psi_-(1) = \psi. \quad (6.52)$$

Then, for the single wall, the free energy per unit area

$$\begin{aligned} \Delta \left( \frac{\beta \Omega}{A} \right) = & \frac{\beta \Omega_{\text{ext}}}{A} (\sigma_S, \psi_S) + \int_0^{\infty} dx \sum_{i=\pm} (\rho_i(x) \ln \left( \frac{\rho_i(x)}{\rho} \right) ) \\ & - (\rho_i(1) - \rho) + \int_0^{\infty} dx \left( \frac{d\psi_i}{dx} \right)^2 \end{aligned} \quad (6.53)$$

which is of the form (6.35), if one identifies  $\psi$  and  $\frac{d\psi}{dx}$  with  $S$  and  $\dot{S}$  and  $\Omega_S$  with  $\Omega_{\text{ext}}$ . Equation (6.38) yields the Poisson-Boltzmann equation. The boundary condition is given by (6.39)

$$\left( \frac{\partial \Omega_{\text{ext}}}{\partial \sigma_S} + \psi_S \right) \delta \sigma_S + \frac{\partial \Omega_{\text{ext}}}{\partial \psi_S} \delta \psi_S = 0. \quad (6.54)$$

This seemingly crude approximation (6.43) for the direct correlation function recovers the familiar expressions for the charge distribution. The expression for the free energy (6.53) is, however, rather cumbersome. This results from its being an expression that can be minimised to give the Poisson-Boltzmann equation. If one is only interested in obtaining the change in free energy in going from one state to another rather than expressing  $\Delta\Omega$  as a functional of the final density, then certain simplifications can be made. To illustrate this, the model equation (6.35) is again used.

Consider  $S'(x)$  varying from the state -

$$S'(x) = 0 \quad \text{all } x \quad (6.55)$$

to the final state

$$S'(x) = S(x) \quad . \quad (6.56)$$

Suppose this is done by changing  $S'(x)$  by infinitesimal changes  $\delta S'(x)$  and at each stage equilibrium is maintained. This may be done by slowly varying the external potential. The change in free energy is then

$$\begin{aligned} \delta \frac{(\Delta\Omega)}{A} &= dx \int_0^{2L} \delta S'(x) \left( \frac{\partial f}{\partial S'} - \frac{d}{dx} \left( \frac{\partial f}{\partial \dot{S}'} \right) \right) \\ &+ \delta S'_w \left( \frac{\partial \Omega}{\partial S'_w} + \frac{\partial f}{\partial \dot{S}'_w} \Big|_w \right) + \delta \dot{S}'_w \frac{\partial \Omega}{\partial \dot{S}'_w} . \end{aligned} \quad (6.57)$$

For equilibrium  $\delta(\Delta\Omega)$  is zero and this implies

$$\frac{\partial f}{\partial S'} = \frac{d}{dx} \left( \frac{\partial f}{\partial \dot{S}'} \right) .$$

Integrating equation (6.57) from  $S'_w = 0$  to  $S'_w = S_w$  yields

$$\frac{\Delta \Omega}{A} = \int_0^{S_w} dS'_w \frac{\partial f}{\partial \dot{S}'_w} \Big|_w + \Omega_S(S_w, \dot{S}_w) . \quad (6.58)$$

For the electric double layer this would mean

$$\frac{\Delta \Omega}{A} = \Omega_{\text{ext}} + \int_0^\sigma \psi_S(\sigma'_S) d\sigma'_S . \quad (6.59)$$

The final step is to use the boundary condition

$$\delta S_w \left( \frac{\partial \Omega_S}{\partial S_w} + \frac{\partial f}{\partial \dot{S}_w} \Big|_w \right) + \delta \dot{S}_w \frac{\partial \Omega}{\partial \dot{S}_w} = 0 . \quad (6.60)$$

If an infinitesimal variation in  $\delta \dot{S}_w$  causes no change in  $\delta S_w$  then the first term must be zero, i.e.

$$\frac{\partial \Omega_S}{\partial S_w} = - \frac{\partial f}{\partial \dot{S}_w} \Big|_w . \quad (6.61)$$

For the electrical double <sup>layer</sup>system this corresponds to the so-called 'constant potential' system and the corresponding equation is

$$\frac{\partial \Omega_{\text{ext}}}{\partial \sigma_S} = - \psi_S . \quad (6.62)$$

Integrating w.r.t. the surface charge yields

$$\Omega_{\text{ext}} = \psi_S \sigma_S + f(\psi_S) \quad (6.63)$$

and

$$\frac{\Delta\Omega}{A} = - \int_0^{\psi_S} \sigma(\psi') d\psi' + f(\psi_S) \quad (6.64)$$

Here  $f$  is some function obtained by the integration.

If, on the other hand, an infinitesimal change in  $\delta S_w$  causes an change in  $\dot{\delta S}_w$ , the second term in (6.60) must be zero, i.e.

$$\frac{\partial\Omega}{\partial\dot{S}_w} = 0 \quad (6.65)$$

For the electrical double layer system this corresponds to the 'constant charge' system and the corresponding equation is

$$\frac{\partial\Omega_{\text{ext}}}{\partial\psi_S} = 0 \quad (6.66)$$

Integrating this w.r.t. the surface potential yields

$$\Omega_{\text{ext}} = g(\sigma_S) \quad (6.67)$$

and

$$\frac{\Delta\Omega}{A} = \int_0^{\sigma_S} \psi_S(\sigma') d\sigma' + g(\sigma_S) \quad (6.68)$$

Equations (6.64) and (6.68) are well-known equations for the

electrical double layer. [5]

## 6.7 Summary

In this chapter we have discussed some aspects of non-uniform systems with particular emphasis on those areas that will be used in the work on liquid crystals. First, we rederive the major integro-differential equations and free energy expressions that describe non-uniform systems. The derivations begin with the ensemble definitions of the grand potential and the single distribution. By doing this, we have eliminated as much formalism as possible and emphasised the physical basis for these equations.

We then discuss the approximations used for the direct and indirect correlation functions, and attempt to describe the physical basis, if any, for these assumptions. Finally, we apply these equations to a model of a familiar system: the colloidal dispersion. Here we derive an expression for the free energy that, when minimised, gives the Poisson-Boltzmann equation. This derivation does not rely on the free energy of mixing of ideal gases. We also show that this expression for the free energy can be simplified to give the more familiar Verwey-Overbeek expressions (6.64) and (6.68) for the free energy. Finally, we give a framework for discussing constant charge and constant potential systems.

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### Appendix 6.1 Translation of the potential field

Consider a small translation  $\Delta \underline{x}$  of the potential field. The new field is

$$\begin{aligned} w(1) &= V_{\text{ext}}(1 + \Delta \underline{x}) \\ &\approx V_{\text{ext}}(1) + \underline{\nabla} V_{\text{ext}}(1) \Delta \underline{x} \end{aligned} \quad (\text{A.1})$$

This results in a new density distribution

$$\begin{aligned} \sigma(1) &\approx \rho(1 + \Delta \underline{x}) \\ &\approx \rho(1) + \underline{\nabla} \rho(1) \Delta \underline{x} \end{aligned} \quad (\text{A.2})$$

By definition

$$\begin{aligned} \sigma(1) &= \sum_{N=1}^{\infty} \frac{e^{\beta \mu N}}{N! h^{3N}} \int d2 \dots dN \int d\rho_1 \dots d\rho_N e^{-\beta[H_0 + \sum_i W(i)]} \times e^{\beta \Omega} \\ &\approx \rho(1) + \Delta \underline{x} \left[ \underline{\nabla} V_{\text{ext}}(1) \rho(1) + \int \underline{\nabla} V_{\text{ext}}(2) \rho(1,2) d2 \right. \\ &\quad \left. - \rho(1) \int d2 \underline{\nabla} V_{\text{ext}}(2) \rho(2) \right] \end{aligned} \quad (\text{A.3})$$

(A.2) and (A.3) imply

$$\begin{aligned} \underline{\nabla} \rho(1) &= -\beta \underline{\nabla} V_{\text{ext}}(1) \rho(1) \\ &\quad - \beta \int d2 \underline{\nabla} V_{\text{ext}}(2) \rho(1) \rho(2) h(1,2) \end{aligned} \quad (\text{A.4})$$

Using the inhomogeneous Ornstein-Zernike eqn.

$$h(1,2) = c(1,2) + \int \rho(3) c(1,3) h(3,2) \quad (\text{A.5})$$

or

$$\nabla \ln \rho(1) = - \beta \nabla V_{\text{ext}}(1) + \int d2 c(1,2) \nabla \rho(2) \quad . \quad (\text{A.6})$$

### Appendix 6.2 Uniform Application of external field

Suppose the external field  $V_{\text{ext}}$  is gradually applied by allowing the parameter in the Hamiltonian

$$H_N = H_0 + \lambda \sum_{i=1}^N V_{\text{ext}}(i) \quad (\text{B.1})$$

to run from 0 to 1. From the definition of the grand potential  $\Omega$  (6.2) and the density distribution  $\rho(1)$  (6.2)

$$\frac{\partial \Omega}{\partial \lambda} = \int d1 V_{\text{ext}}(1) \rho_{\lambda}(1) \quad (\text{B.2})$$

$$\frac{\partial \rho_{\lambda}(1)}{\partial \lambda} = - \beta V_{\text{ext}}(1) \rho(1) - \beta \int d2 V_{\text{ext}}(2) \rho(2) h(1,2) \rho(1) \quad . \quad (\text{B.3})$$

Using the inhomogeneous Ornstein-Zernike equation (A.5) gives

$$\frac{\partial \ln \rho_{\lambda}(1)}{\partial \lambda} = - \beta V_{\text{ext}}(1) + \int d2 c_{\lambda}(1,2) \frac{\partial \rho_{\lambda}}{\partial \lambda}(2) \quad (\text{B.4})$$

Substituting (B.4) into (B.2) gives

$$\frac{\partial(\Omega\beta)}{\partial\lambda} = \int d1 \left\{ -\frac{\partial\rho_\lambda}{\partial\lambda} + \int d2 c_{\lambda(1,2)} \frac{\partial\rho_{\lambda(2)}}{\partial\lambda} \rho(1) \right\} . \quad (\text{B.5})$$

### Appendix 6.3 Free energy expression

Suppose the density follows the path

$$\rho_\alpha(1) = \rho_0 + \alpha (\rho(1) - \rho_0) \quad (\text{C.1})$$

and the Hamiltonian needed to do this is

$$H_N = H_0 + \sum_i V_{\text{ext}}(i) \lambda(i, \alpha) \quad (\text{C.2})$$

where

$$\lambda(i, 0) = 0 \quad (\text{C.3})$$

and

$$\lambda(i, 1) = 1 . \quad (\text{C.4})$$

In a similar manner to Appendix (6.2) the following equations can be derived

$$\frac{\partial\Omega}{\partial\alpha} = \int V_{\text{ext}}(1) \frac{\partial\lambda}{\partial\alpha}(1) \rho_\alpha(1) d1 \quad (\text{C.5})$$

$$\begin{aligned}
 \rho(1) - \rho_0 &= \frac{\partial \rho_\alpha}{\partial \alpha} = -\beta V_{\text{ext}}(1) \frac{\partial \lambda}{\partial \alpha}(1) \rho_\alpha(1) \\
 &+ \int d2 c_\alpha(1,2) \frac{\partial \lambda_\alpha}{\partial \alpha}(2) \rho_\alpha(1)
 \end{aligned}
 \tag{C.6}$$

Rewriting this gives

$$\begin{aligned}
 \beta V_{\text{ext}}(1) \frac{\partial \lambda}{\partial \alpha}(1) \rho_\alpha(1) &= -[\rho(1) - \rho_0] \\
 &+ \int d2 c_\alpha(1,2) [\rho(2) - \rho_0] \\
 &\times [\rho_0 + \alpha(\rho(1) - \rho_0)]
 \end{aligned}
 \tag{C.7}$$

Substituting this into (C.5) gives Evan's result

$$\begin{aligned}
 \Delta(\beta\Omega) &= \int d1 \int_0^1 d\alpha \alpha [\rho(1) - \rho_0] \left\{ \int d2 c_\alpha(1,2) [\rho(2) - \rho_0] - 1 \right\} \\
 &+ \rho_0 \int_0^1 d\alpha \int d1 \int d2 c_\alpha(1,2) [\rho(2) - \rho_0] .
 \end{aligned}
 \tag{C.8}$$

Alternatively one can integrate (C.7) to give

$$\begin{aligned}
 \beta V_{\text{ext}}(1) \lambda(\alpha) &= -\ln \left[ 1 + \frac{\alpha(\rho(1) - \rho_0)}{\rho_0} \right] \\
 &+ \int_0^\alpha d\alpha' \int d2 c_\alpha(1,2) [\rho(2) - \rho_0]
 \end{aligned}
 \tag{C.9}$$

and integrate (C.5) by parts to give

$$\Delta(\beta\Omega) = \int d1 V_{\text{ext}}(1) \rho(1) \beta - \int d1 \int_0^1 d\alpha V_{\text{ext}}(1) \lambda(\alpha) \beta(\rho(1) - \rho_0) \tag{C.10} .$$

Substituting (C.9) into (C.10) gives Saam & Ebner's result

$$\begin{aligned}\Delta(\beta\Omega) &= \int dl \, v_{\text{ext}}(l) \, \rho(l) \\ &+ \int dl \, \rho(l) \, \ln \left( \frac{\rho(l)}{\rho_0} \right) - [\rho(l) - \rho_0] \\ &- \int dl \int_0^1 d\alpha \int d2 \int_0^\alpha d\alpha' \, c_\alpha(1,2) [\rho(2) - \rho_0] [\rho(l) - \rho_0] \, .\end{aligned}$$

Finally putting  $\alpha = 1$  in (C.9) gives

$$\begin{aligned}\beta v_{\text{ext}}(l) &= - \ln (\rho(l)/\rho_0) \\ &+ \int_0^1 d\alpha \int d2 \, c_\alpha(1,2) [\rho(2) - \rho_0] \, .\end{aligned}$$

#### Appendix 6.4 Landau Expansion

From Appendix 6.3

$$\begin{aligned}\Delta\Omega &= \int dl \, v_{\text{ext}}(l) \, \rho(l) + \int dl \, \rho(l) \, \ln \left( \frac{\rho(l)}{\rho_0} \right) - [\rho(l) - \rho_0] \\ &- \int dl \int d2 \, \bar{c}(1,2) [\rho(2) - \rho_0] [\rho(l) - \rho_0]\end{aligned}$$

where

$$\bar{c}(1,2) = \int_0^1 d\alpha \int_0^\alpha d\alpha' c_\alpha(1,2) \quad .$$

The last term can be written in terms of the Fourier transforms of the various quantities. If the effect of the external potential is linearised

$$I = - \int \frac{d\mathbf{k}}{(2\pi)^3} \hat{h}(-\mathbf{k}) \hat{c}(\mathbf{k}) \hat{h}(\mathbf{k})$$

where

$$\hat{f}(\hat{\mathbf{k}}) = \int d\mathbf{r} e^{i\hat{\mathbf{k}} \cdot \mathbf{r}} f(\mathbf{r}) \quad .$$

If  $c(1,2)$  is short-ranged

$$\hat{c}(\mathbf{k}) \approx \hat{c}(0) + \frac{1}{2} k^2 \frac{\partial^2 \hat{c}}{\partial k^2}(0)$$

where to this order of the density expansion

$$\hat{c}(0) = \int d\mathbf{r} \int_0^1 d\alpha \int_0^\alpha d\alpha' c_\alpha(1,2)$$

$$= \frac{1}{2} \int d\mathbf{r} c_{\text{bulk}}(\mathbf{r})$$

$$= \frac{\hat{c}_{\text{bulk}}(0)}{2} \quad .$$

Similarly

$$\hat{c}''(0) = \hat{c}_{\text{bulk}}''(0)/2 \quad .$$

From the inverse transform

$$\begin{aligned} \therefore I &= -\frac{1}{2} \hat{c}_{\text{bulk}}(0) \int dl (\rho(l) - \rho_0)^2 \\ &\quad - \frac{1}{4} \hat{c}_{\text{bulk}}''(0) \int dl (\nabla \rho(l))^2 \quad . \end{aligned}$$

To this order in density expansion

$$\Delta\Omega = \int dl f_0(\rho(l)) + (\nabla \rho(l))^2 f_2(\rho(l))$$

where

$$\begin{aligned} f_0(\rho) &= V_{\text{ext}} \rho + \rho \ln \left( \frac{\rho}{\rho_0} \right) \\ &\quad - [\rho - \rho_0] - \frac{\hat{c}}{2} \text{bulk}(0) (\rho - \rho_0)^2 \end{aligned}$$

$$f_2(\rho) = -\frac{\hat{c}''}{4} \text{bulk}(0).$$

## CHAPTER 7

### LIQUID CRYSTALS

#### 7.1 Introduction

In this chapter, an expression for the free energy of a liquid crystal system is developed. This expression is related to molecular properties by the direct correlation function  $c(1,2)$ . From the expression of the free energy, one can make predictions about the isotropic-nematic transition and properties of liquid crystals under stress.

This work begins with a discussion of the molecular properties of liquid crystals and its relevance to the form of the correlation function. From this, an expression for the free energy is developed. The qualitative features of this free energy are described in terms of the temperature and the order parameter in section 7.3. The minimisation of the free energy yields an expression for the density distribution in terms of the direct correlation function  $c$ . Thus one can obtain the expression for the pseudopotential (section 2.4). Some reasonable assumptions lead to the well-known Maier-Saupe theory. The form of the free energy suggests possible generalisations of the Maier-Saupe theory.

The basis of these approximations is the use of the notion that the local structure in the isotropic and nematic phases are very similar. This means that locally, a short-ranged function such as the direct correlation function is the same in both phases on the microscopic level. This allows certain simplifications to be made.

The final section of the chapter deals with non-uniform systems. First, the elastic constants of a nematic are calculated using the derivation of Stecki et al [1]. Next the effect of surface ordering is investigated using the techniques developed in the last chapter.



## 7.2 Molecular Properties

In developing a theory for the isotropic-nematic transition, only those molecular properties essential to forming a nematic phase will be considered. Complications can be included later.

The molecules of all liquid crystals are elongated. This results in both the short-range repulsions and longer-ranged attractions becoming strongly anisotropic. It is this anisotropy that causes the isotropic-nematic transition. For the purpose of describing the repulsive component of the intermolecular potential, the molecule is modelled as a hard or soft, rigid, rod-shaped particle. The molecules of most liquid crystals have some flexibility which can be important in determining macroscopic properties [2]. However, not all liquid crystals have flexible molecules and it seems that some degree of rigidity is needed to form a stable nematic phase [3]. Thus, for simplicity, total rigidity is assumed.

Most liquid crystals are polar. The dipole moment of the molecule seems to enhance the stability of the nematic phase, but is not essential for its formation [3]. For simplicity, it is assumed that the molecule has no permanent dipole moment although it is not difficult to include the effect of the dipole.

Thus, in order to investigate liquid crystals, a system of elongated, nonpolar rigid particles which interact via anisotropic van der Waals forces will be studied. It is assumed that the particles are cylindrically symmetric and have the added symmetry that neither end of the molecule is distinguishable.

It was shown in Chapter 2 that the direct correlation function for an aligned system of cylindrically symmetric molecules can be

expanded

$$c(1,2) = \sum_{\substack{mnl \\ \mu\nu}} c_{\mu\nu}^{mnl}(r) \psi_{\mu\nu}^{mnl}(\omega_1, \omega_2, \hat{\underline{r}}, \hat{\underline{z}}) \quad (7.1)$$

where

$$\begin{aligned} \psi_{\mu\nu}^{mnl}(\omega_1, \omega_2, \hat{\underline{r}}, \hat{\underline{z}}) \\ = D_{o\mu}^{*M}(\omega_1) D_{o\nu}^n(\omega_2) D_{o\lambda}^\ell(\hat{\underline{r}}) \delta_{\lambda, \mu - \nu} \end{aligned}$$

Here  $\omega_i$  is the orientation of molecule  $i$ ,  $\underline{r}$  the orientation of the intermolecular axes w.r.t. the bulk director, and  $r$  is the intermolecular separation. Because there is no difference between a director  $\hat{\underline{n}}$  and direction antiparallel to it,  $m$  and  $n$  are even.

### 7.3 Order Parameter

As in the system of dipoles affected by an external field, the number density of particles whose axes lie at an angle  $\theta$  to the bulk director is described by a function  $\rho(\theta)$ :

$$\begin{aligned} \rho(\theta) &= \rho_0 \sum (2\ell+1) S_\ell P_\ell(\cos\theta) \\ &= \rho_0 \int_0^\pi (1 + 5S_2 P_2(\cos\theta) + 7S_4 P_4(\cos\theta) + \dots) \sin\theta d\theta \end{aligned} \quad (7.2)$$

Here  $\rho_0$  is the bulk density of the isotropic phase at some reference temperature  $T_{\text{ref}}$ . The terms  $S_\ell$  are given by

$$S_\ell = \int_0^1 \frac{\rho(\theta)}{\rho_0} P_\ell(\cos\theta) d(\cos\theta) \quad . \quad (7.3)$$

The term  $S$  is called the order parameter and is important in describing the nematic phase. For the temperature range of concern, the change in density is small and  $S_0$  is negligible. The higher terms  $S_6, S_8 \dots$  are expected to be small. For a disordered phase (isotropic phase)

$$S_2 = 0$$

and for a totally aligned fluid

$$S_2 = 1 \quad .$$

At times when only  $S_2$  is considered the subscript will be dropped.

#### 7.4 Temperature Dependence of the Free Energy

In Chapter 6, the concept of a generalised free energy  $\Delta\Omega'$  as a functional of the density distribution  $\rho'(1)$  was introduced. When  $\Delta\Omega'$  is minimised with respect to  $\rho'(1)$  the minimum value obtained is the change in grand potential  $\Delta\Omega$  and the minimising distribution is the equilibrium distribution  $\rho(1)$ . The same concept can be applied to the bulk nematic system in that a generalised free energy  $\Delta\Omega'$  can be expressed as functional of  $\rho'(0)$ . Suppose that this generalised free energy  $\Delta\Omega'$  depended only on the order parameters  $S$ . Then it is expected that  $\Delta\Omega'(S)$  would have the following qualitative features.

If the temperature  $T$  is high enough, the stable phase is the isotropic liquid and no metastable phase exists (see Fig. 7.1(a)).

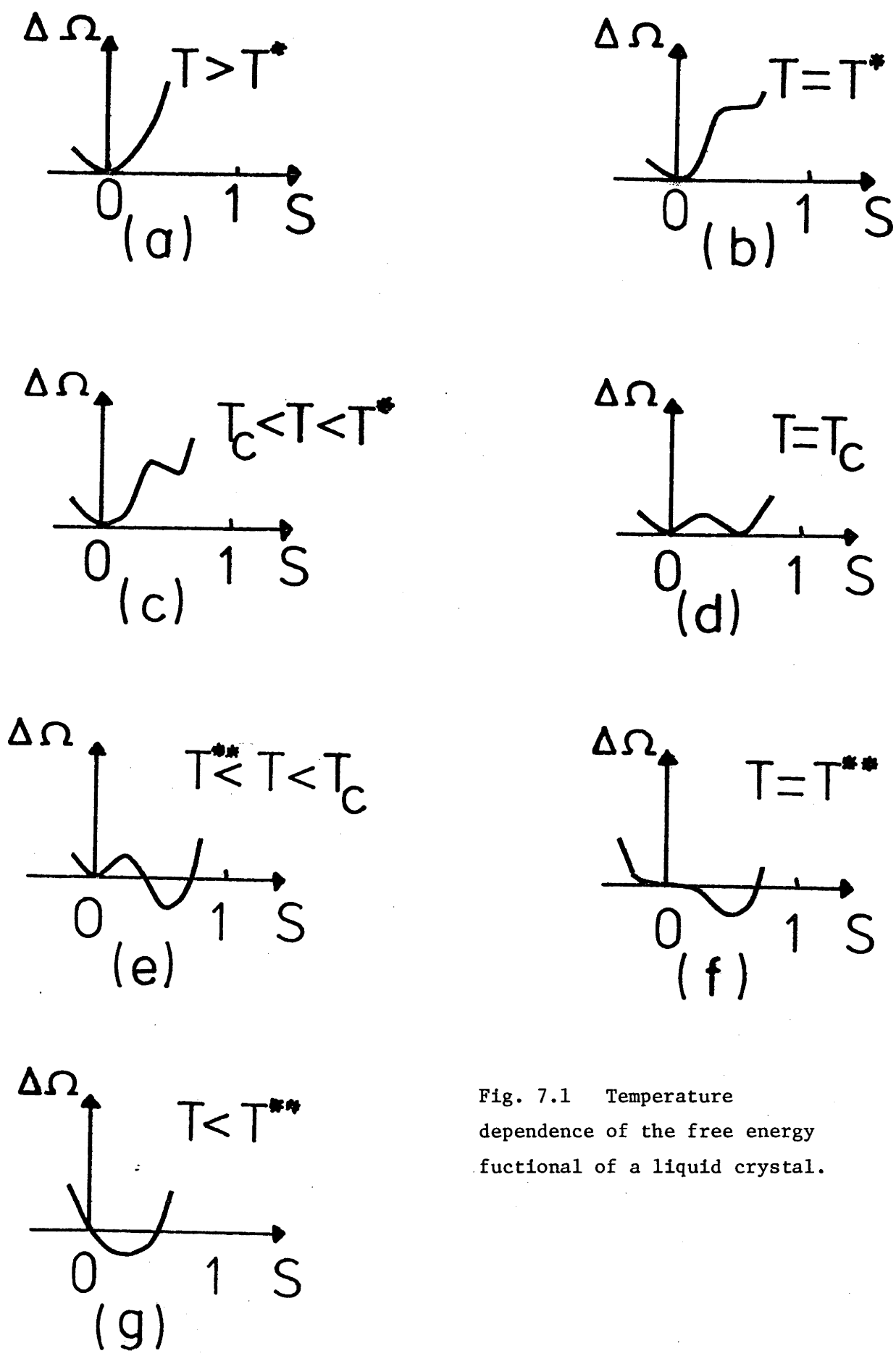


Fig. 7.1 Temperature dependence of the free energy functional of a liquid crystal.

As the temperature falls, a second minimum in the free energy develops. This corresponds to a metastable nematic phase. At  $T = T_c$ , the nematic phase becomes the stable phase.  $T^*$  and  $T^{**}$  are the temperatures at which the second minimum corresponding to the metastable states respectively begins and ends as the temperature drops.

#### 7.4 Isotropic-Nematic Transition

In this section the free energy of a phase transition will be calculated, and the notion of a pseudopotential will be introduced. This will be the basis of the rest of the chapter.

For the isotropic-nematic transition, only the temperature range  $T^* < T < T^{**}$  need be considered, i.e. the range in which a metastable phase exists. Suppose that for  $T_c < T < T^{**}$  an external field is applied to the stable isotropic phase and that while this external field is uniform in position, it is not in orientation. Thus, it affects the orientation of the molecules. Suppose further that it is gradually applied in such a way that its effect on the generalised free energy of the system is that illustrated in Fig. 7.2. The system gradually transforms from the isotropic phase to an ordered phase. Suppose that the external potential  $V_{\text{ext}}$  is such that the order parameter is the same as the previously metastable state. In section 6.2 it is shown

$$\Delta(\beta\Omega) = \int_0^1 d(\cos\theta) (\rho(\theta) - \rho_0) V_{\text{ext}}(\theta) + \int_0^1 d(\cos\theta) \left[ \rho(\theta) \ln \left( \frac{\rho(\theta)}{\rho_0} \right) - (\rho(\theta) - \rho_0) \right]$$

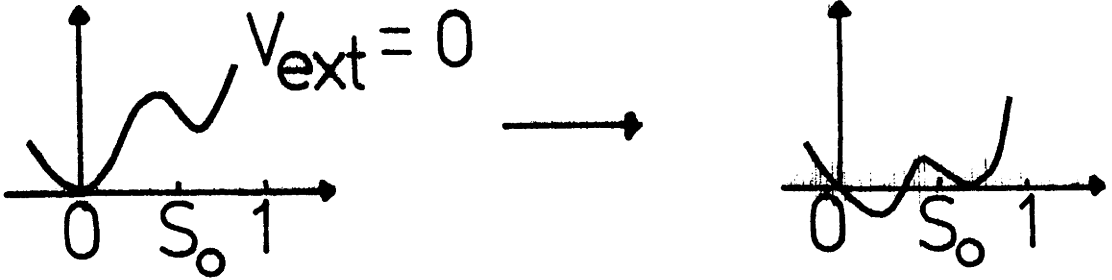


Fig. 7.2 The effect of a certain external field on the free energy functional of a liquid crystal. The order parameter of the final density distribution is the same as that of the previously metastable nematic phase.

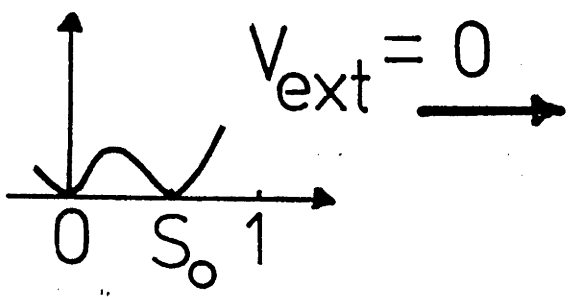
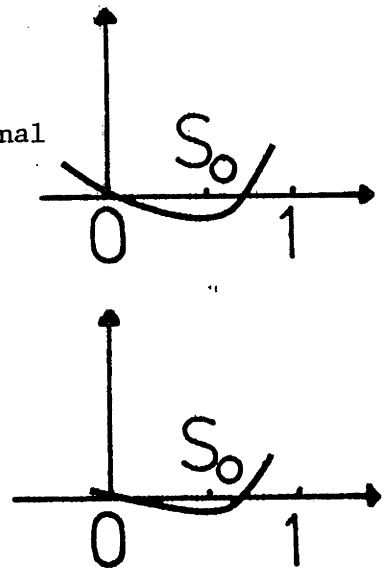
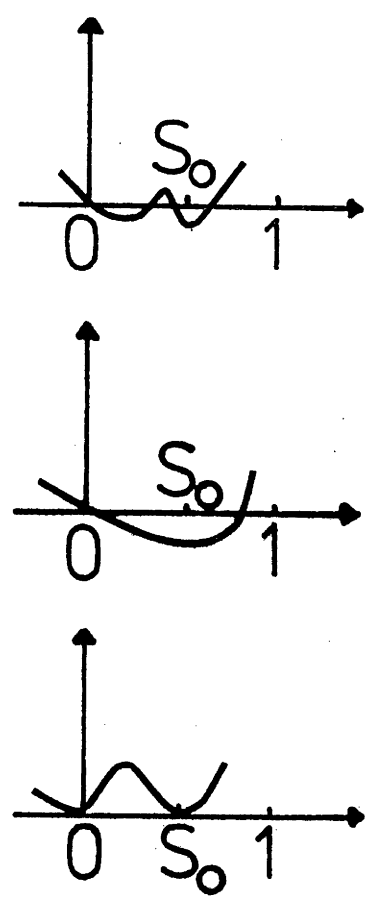


Fig. 7.3 As for Fig. 7.2, but the temperature is closer to  $T_c$ .



$$\begin{aligned}
& - \frac{1}{4\pi^2} \int_0^1 d(\cos\theta) \int_0^1 d(\cos\theta') \int_0^{2\pi} \int_0^{2\pi} d\phi d\phi' \\
& \int_0^1 d\alpha \int_0^\alpha d\alpha' \int_0^1 d\underline{r} c_\alpha(1,2) (\rho(\theta') - \rho_0)(\rho(\theta) - \rho_0) , \quad (7.4)
\end{aligned}$$

where the Euler angles for molecules 1 and 2 are respectively  $(\phi, \theta, \chi)$ ,  $(\phi', \theta', \chi')$ ,  $c_\alpha(1,2)$  the direct correlation function of a system in which the density is

$$\rho(1) = \rho_0 + \alpha(\rho(1) - \rho_0) \quad (7.5)$$

and  $\Omega$  is the grand potential (6.2). Hereafter the notation

$$\bar{c}(\theta, \theta') = \frac{1}{2\pi^2} \int_0^1 d\alpha \int_0^\alpha d\alpha' \int_0^{2\pi} \int_0^{2\pi} c_\alpha(1,2) d\underline{r} d\phi d\phi' \quad (7.6)$$

will be used. Some care must be taken with expression (7.4). The external potential is assumed to be applied in such a way that (7.5) holds. However, except at the phase transition itself, the change in free energy is independent of the path taken. The expression (7.4) is minimised by the density

$$\begin{aligned}
\ln \frac{\rho(\theta)}{\rho} &= -\beta \int_0^1 V_{\text{ext}}(\theta) \rho(\theta) d(\cos\theta) \\
&+ \int_0^1 d(\cos\theta) \bar{c}(\theta, \theta') (\rho(\theta) - \rho_0) . \quad (7.7)
\end{aligned}$$

At each temperature, a similar process can be applied. As  $T \rightarrow T_c$ , consider  $V_{\text{ext}}(1)$  to be applied in such a way that the free energy changes as illustrated in Fig. 7.3. The order parameter of the system gradually changes from 0 to the order parameter  $S_0$  of the nematic system and yet the final external field is zero in the limit as  $T \rightarrow T_c$ . The expression (7.7) would then give

$$\ln \left( \frac{\rho(\theta)}{\rho_0} \right) = \int_0^1 d(\cos\theta') \bar{c}(\theta, \theta') (\rho(\theta') - \rho) \quad (7.8a)$$

$$= -\beta U_0 - \beta U_2 P_2(\cos\theta) - \beta U_4 P_4(\cos\theta) + \dots \quad (7.8b)$$

$$U_\ell = -kT \int_0^1 d(\cos\theta') \int_0^1 d(\cos\theta) \bar{c}(\theta, \theta')$$

$$(\rho(\theta') - \rho) P_\ell(\cos\theta) (2\ell + 1) \quad (7.9)$$

The term

$$U = U_0 + U_2 P_2(\cos\theta) + U_4 P_4(\cos\theta) + \dots \quad (7.10)$$

is called the pseudo-potential. The equation (7.8b) is often the starting point of mean field theories. Thus this procedure developed here gives an explicit expression for  $U$  in terms of the direct correlation function. The main problem is finding an expression for the direct correlation function.

One approximation for the direct correlation function is the low density limit

$$c(1,2) \rightarrow \exp(-\beta u(1,2)) - 1 \quad (7.11)$$



Here  $u(1,2)$  is the intermolecular potential. Onsager [4] considered the molecules of the liquid crystals as hard rods. In the approximation (7.11) this would imply

$$c(1,2) = \begin{cases} -1 & \text{if molecules 1 and 2 overlap.} \\ 0 & \text{if molecules 1 and 2 do not overlap.} \end{cases}$$

Thus

$$\bar{c}(\theta, \theta') = -V_{\text{excl}}(\theta - \theta') \quad (7.12)$$

where  $V_{\text{excl}}$  is the so-called 'excluded volume'. This is the volume about the centre of one molecule in which another molecule, whose axis makes an angle  $\theta - \theta'$  with the first molecule, cannot be situated without some overlapping occurring. For two cylindrical rods of length  $L$  and diameter  $D$

$$V_{\text{excl}} = 2L^2D|\sin(\theta - \theta')| \quad L \gg D.$$

The free energy can be written

$$\begin{aligned} \Delta(\beta\Omega) = & \int d(\cos\theta) (\rho(\theta) \ln \left( \frac{\rho(\theta)}{\rho_0} \right)) \\ & + \frac{1}{2} \int (\rho(\theta) - \rho_0)(\rho(\theta') - \rho_0) V_{\text{excl}}(\theta - \theta') d(\cos\theta)d(\cos\theta') \quad (7.13) \end{aligned}$$

Minimisation of the free energy leads to a first order phase transition. The order parameter  $S_c$  at the temperature  $T_c$  is predicted to be approximately 0.8. For most liquid crystals  $S_c \approx .4$ .

### 7.5 Local Structure

Near  $T_c$ , the local structure of the isotropic phase is similar to that of the nematic phase. The notion of a local director was introduced in section 1.7 and it was postulated that in both phases the local director meanders. However, in the isotropic phase there is no long-ranged correlation. An orientational probability function  $g(\theta)$  can be used to describe the orientation of the local director with respect to the bulk director:  $g(\theta)d\theta \equiv$  probability that the angle between the local director and the bulk director lies in the range  $\theta$  and  $\theta+d\theta$ . Another orientation distribution function  $h(\theta)$  can be used to describe the number density of molecules whose axis lies at an angle  $\theta$  to the local director. The bulk number density  $\rho(\theta)$  can then be written in terms of  $g(\theta)$  and  $h(\theta)$ .

Suppose at a particular time, the local director at  $\underline{r}$  has an orientation  $\omega_n$  with respect to the bulk director. The number of density particles, the axes of which lie at an angle  $\theta$  with respect to this local director is

$$h(\theta) = \rho_0 \left( 1 + \sum_{L=2}^{\infty} h_L P_L(\cos\theta) \right) \quad (7.14)$$

$$= \rho_0 \left( 1 + \sum_{L=2}^{\infty} h_L \sum_{M=-L}^L D_{oM}^L(\omega_1) D_{Mo}^L(\omega_n) \right) \quad (7.15)$$

where  $\omega_1$  is the orientation of molecule 1 with respect to the bulk director. The number density of particles at  $\underline{r}$  with an orientation  $\omega_1$  w.r.t. the bulk direction is given by

$$\rho(\omega_1, \omega_n) = \rho \sum_{L=2}^{\infty} \left( 1 + \sum_{M=-L}^L h_{LM} D_{0M}^L(\omega_1) \right) \quad (7.16)$$

$$h_{LM} = h_L D_{M0}^L(\omega_n) \quad (7.17)$$

Then

$$\rho(\theta) = \frac{1}{2\pi^2} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta g(\theta) \rho(\omega_1, \omega_n) \quad (7.18)$$

where

$$\omega_n = (\phi, \theta, \chi) \quad \omega_1 = (\phi', \theta', \chi')$$

Finally, using (7.16), (7.17), (7.18)

$$\rho(\theta) = \rho_0 \left( 1 + \sum_{L=2}^{\infty} h_L g_L P_L(\cos\theta') \right) \quad (7.19)$$

$$g_L = \frac{1}{\pi} \int_0^{\pi} d\theta g(\theta) P_L(\cos\theta) \quad (7.20)$$

Thus

$$S_2 = h_2 g_2 \quad (7.21)$$

Since the direct correlation function is expected to be short-ranged and hence dependent only on local structure it should be suitable for a similar analysis. The direct correlation function  $c(1,2)$  of the bulk liquid crystal can be expanded (Chapter 2)

$$c(1,2) = \sum_{\text{oo}} c^{\text{mnl}}(\mathbf{r}) \psi_{\text{oo}}^{\text{mnl}}(\omega_1, \omega_2, \hat{\mathbf{r}}) \quad (7.22a)$$

for the isotropic phase and

$$c(1,2) = \sum c_{\mu\nu,nem}^{mnl}(r) \psi_{\mu\nu}^{mnl}(\omega_1, \omega_2, \hat{r}, \hat{z}) \quad (7.22b)$$

for the nematic phase. It is expected that the direct correlation function of a microscopic volume ( $\approx 20$  molecules) about the local director is cylindrical symmetric about the local director and thus can be expanded

$$c_{loc}(1,2) = \sum c_{\mu\nu,loc}^{mnl}(r) \psi_{\mu\nu}^{mnl}(\omega_1, \omega_2, \hat{r}, \hat{\omega}_n) \quad (7.22c)$$

It is shown in Appendix 1 that

$$c_{iso}^{mnl}(r) = \sum_{\mu,\nu} c_{\mu\nu,loc}^{mnl}(r) \begin{pmatrix} m & n & 1 \\ \mu & -\nu & -\lambda \end{pmatrix} (-)^{\mu} \quad (7.23a)$$

$$\begin{aligned} c_{-\mu',\nu',nem}^{mnl}(r) &= c_{iso}^{mnl}(r) \begin{pmatrix} m & n & 1 \\ -\mu' & \nu' & \lambda' \end{pmatrix} (-1)^{\mu'} \\ &+ \sum_{\mu,\nu} c_{\mu\nu,loc}^{mnl}(r) \sum_{L=2}^{\infty} h_L (-)^{\mu+\mu'+\lambda'+\lambda} \\ &\sum_P \begin{pmatrix} l & L & P \\ \lambda' & 0 & -\lambda' \end{pmatrix} \begin{pmatrix} l & L & P \\ \lambda & 0 & -\lambda \end{pmatrix} \delta_{\lambda,\mu-\nu} \begin{pmatrix} m & n & P \\ \mu' & n' & \lambda' \end{pmatrix} \begin{pmatrix} m & n & P \\ -\mu & \nu & \lambda \end{pmatrix} \quad (7.23b) \end{aligned}$$

Of particular interest is the term

$$\bar{c}_{oo}^{220} = \int_0^1 dx P_2(x) \int_0^1 dx' P_2(x') \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' \int d\tilde{r} \bar{c}(1,2)$$

where the notation is that used in the previous section. It is shown in Appendix 1 that

$$c_{oo,nem}^{220} = c_{iso}^{220} + \sum_{\mu} c_{\mu\mu,loc}^{220} \frac{h_2}{5} (-)^{\mu}$$

$$\begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 2 & 2 & 2 \\ -\mu & \mu & 0 \end{pmatrix} + \sum_{L=4}^{\infty} (\dots\dots\dots) . \quad (7.23c)$$

## 7.6 Isotropic-Nematic Transition (Revisited)

Equation (7.7b) can be written as

$$\rho(\theta) = \rho_0 \exp(-\beta V(x)) \quad (7.24a)$$

$$x = \cos\theta . \quad (7.24b)$$

The order parameters are then

$$S_{\ell} = \int_{-1}^1 dx e^{-\beta U(x)} P_{\ell}(x) . \quad (7.25)$$

The change in density at the transition is very small and shall be ignored. However, the effect of the change in density is easily included if needed (7.25) can then be written

$$S_{\ell} = \frac{\int_0^1 dx e^{-\beta U(x)} P_{\ell}(x)}{\int_0^1 dx e^{-\beta U(x)}} \quad (7.26)$$

The change in free energy can be written

$$\Delta(\beta\Omega) = - \int dx \frac{1}{2} \beta \left( \sum_L U_L S_L \right) - \ln z \quad (7.27a)$$

$$z = \int_0^1 dx e^{-\beta U(x)} P(x) . \quad (7.27b)$$

Some further assumptions need to be made. It is expected that  $S_6, S_8$ , etc are small and thus shall be ignored. Moreover the approximation (section 7.5) of the local structure of the 2 phases being the same leads to

$$U_2 = V_1 S_2 + V_2 S_2^2 + V_3 S_4 S_2 + \dots \quad (7.28a)$$

$$U_4 = W_1 S_4 + W_2 S_2 S_4 + W_3 S_4^2 + \dots \quad (7.28b)$$

where

$$V_1 = -kT \int_0^\infty c_{iso}^{220}(r) r^2 dr \quad (7.29a)$$

$$W_1 = -kT \int_0^\infty c_{iso}^{440}(r) r^2 dr \quad (7.29b)$$

$$V_2 = -kT \int_0^\infty c_{\mu\mu,loc}^{220}(r) r^2 \frac{dr(-)^\mu}{5} \begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 2 & 2 & 2 \\ -\mu & \mu & \mu \end{pmatrix} \quad (7.30a)$$

$$W_2 = -kT \int_0^\infty c_{\mu\mu,loc}^{420}(r) r^2 \frac{dr(-)^\mu}{5} \begin{pmatrix} 4 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 4 & 2 & 2 \\ -\mu & \mu & 0 \end{pmatrix} \quad (7.30b)$$

The terms  $V_3, W_3$  are similar to  $V_2, W_2$ .

The approximation

$$V_2 = V_3 = \dots = 0 \quad (7.31a)$$

$$W_1 = W_2 = W_3 = \dots = 0 \quad (7.31b)$$

leads to the well-known Maier-Saupe [5] theory. In this approximation the equations (7.24a), (7.27a), (7.27b) become

$$\rho(\theta) \approx \rho_0 \exp(-\beta V_2 P_2(x)) \quad (7.32)$$

$$\Delta\Omega \approx -\frac{1}{2} \beta V_2 S_2^2 - \ln Z \quad (7.33)$$

$$Z = \int_0^1 dx e^{-\beta V_2 S_2^2 P_2(x)} \quad (7.34)$$

When  $\Delta\Omega$  (7.33) is minimised w.r.t.  $S_2$  a first order phase transition is predicted with

$$\frac{kT}{V_2(T_c)} = \frac{1}{4.55} \quad (7.35a)$$

and

$$S_2^c = .45 \quad (7.35b)$$

for all  $V_2$  and thus for all nematic-isotropic transitions. Here  $S_2^c$  is the second order parameter at the critical point. If  $V_2$  is assumed to be independent of temperature, then the Maier-Saupe theory predicts second order parameters in qualitative agreement with experiment. The fit to experimental data is remarkable considering that the original derivation [5] contributed the total interaction to van der Waals attraction. This would produce an energy an order of magnitude too small to provide the right parameter to fit experiments.

Humphries et al [6] have improved the results by including the term  $W_1$ . The effect of the term  $V_2$  is now being investigated. This can be done by trying to calculate  $c_{\mu\nu,loc}^{mnl}(r)$  and use these to calculate  $V_1, W_1$ . Alternatively one can fit the parameters  $V_1, V_2$  and  $W_1$  to

experiments. As the number of parameters is increased the fit to experimental data must improve without necessarily any physics being added. For this reason, one would like to use the former method but if the parameter fit can show consistency with experiments different from those used in the fit, then this should be sufficient.

### 7.7 Landau - de Gennes Expansion

de Gennes [ 7 ] considered an expansion of the form

$$\Delta\Omega = a(T - T_0)S^2 + bS^3 + cS^4 + o(S^4) \quad (7.39)$$

where  $T_0$  is close to  $T_c$  and  $b, c$  are relatively independent of temperature. An expansion of this form can with the right parameters produce the behaviour seen in Fig. 7.1(a)-(g). Using experimental results, the parameters in the (7.39) have been deduced for some substances (see e.g. [8,9]).

The expansion (7.39) is useful for studying fluctuations in the isotropic phase [7] and if adopted to be an expansion in  $(S - S_c)$  is useful for studying fluctuations in the nematic phase.

Expanding the Maier-Saupe expression for the free energy

$$\Delta\Omega = \frac{1}{2} \beta U (S+1) - \log \int_0^1 \exp \left( \frac{3}{2} \beta U S x^2 \right) dx \quad (7.40)$$

in  $S$  yields

$$\Delta\Omega = S^2 \frac{U}{2T} (T - T_0) - \frac{S^3 U^3}{6K^2 T^2} \begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} + o(S^4) \quad (7.41)$$



$$\Delta\Omega = a (T - T_0)S^2 + b S^3 + O(S^4) \quad (7.42)$$

$$a = \frac{U}{2T_c} \quad b = \frac{U^3}{6k^2T_c^2} \begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \quad T_0 = \frac{4.555}{5} \quad (7.43)$$

Any expression of the form (7.24) can be expanded in this way and compared with experimental data.

## 7.8 Elastic Constants

Stresses applied to liquid crystals can lead to bending, splaying and twisting of the director. (See Fig. 1.16). This caused a change in the free energy given by

$$\begin{aligned} \Delta\Omega = & \int d\mathbf{l} \beta V_{\text{ext}}(\mathbf{l}) (\rho(\mathbf{l}) - \rho_0(\omega)) + \int d\mathbf{l} \ln \left( \frac{\rho(\mathbf{l})}{\rho_0(\omega)} \right) \\ & - [\rho(\mathbf{l}) - \rho_0(\omega_1)] - \frac{1}{2} \int d\mathbf{l} \int d\mathbf{2} \bar{c}(\mathbf{l}, \mathbf{2}) [\rho(\mathbf{2}) - \rho_0(\omega_2)] \\ & [\rho(\mathbf{l}) - \rho_0(\omega_1)] \end{aligned} \quad (7.45)$$

where  $\bar{c}(\mathbf{l}, \mathbf{2}) = \int_0^1 d\alpha \int_0^\alpha d\alpha' c_\alpha(\mathbf{l}, \mathbf{2})$ . Here  $c_\alpha$  is the direct correlation function of a system in which the density is

$$\rho_\alpha(\mathbf{l}) = \rho_0(\omega_1) + \alpha(\rho(\mathbf{l}) - \rho_0(\omega_1))$$

and  $V_{\text{ext}}$  is the external potential. If these distortions of the director have a long wavelength, the density distribution about the director is approximately constant. Stecki et al [1] expressed this as

$$\rho(\mathbf{l}) = \rho_0(\hat{\mathbf{n}}(\mathbf{x}_1) \cdot \omega_1) \quad (7.46)$$

where  $\rho_0(\cos\theta)$  is the number density,  $\hat{n}$  the bulk director and  $\omega_1$  the orientation of molecule 1. For distortion of this type, only the last term in (7.45) is affected. Using a Landau expansion, the change in free energy can be written

$$\Delta\Omega = \frac{1}{4} \int d\mathbf{l} \, \bar{c}_{\alpha\beta} \partial_\alpha \rho(1) \partial_\beta \rho(2) \quad (7.47)$$

$$\text{where } \bar{c}_{\alpha\beta} = \int d\mathbf{r} \, r_\alpha r_\beta \bar{c}(\mathbf{r}, \omega_1, \omega_2) \quad (7.48)$$

Using (7.46)

$$\partial_\alpha \rho(1) = \rho'_0(\cos\theta_1) \partial_\alpha n_\gamma \omega_\gamma^1 \quad (7.49)$$

one obtains

$$\Delta\Omega = \frac{1}{4} \bar{c}_{\alpha\beta\gamma\delta} \partial_\alpha n_\gamma \partial_\beta n_\delta \quad (7.50)$$

$$\begin{aligned} \bar{c}_{\alpha\beta\gamma\delta} &= \int d\mathbf{r} \int d\omega_1 \int d\omega_2 \, r_\alpha r_\beta \bar{c}(\mathbf{r}, \omega_1, \omega_2) \\ &\quad \rho'_0(\cos\theta'_1) \rho_0(\cos\theta_2) \omega_\gamma^1 \omega_\delta^2 \end{aligned} \quad (7.51)$$

In principle there are 81 terms. However terms involving  $n_z$  are negligible (where  $z$  is parallel to the original bulk director) and this reduces the number to 36. Furthermore

$$\begin{aligned} \bar{c}_{\alpha\beta\gamma\delta} &= \bar{c}_{\alpha\beta\delta\gamma} \\ \bar{c}_{\alpha\beta\gamma\delta} &= \bar{c}_{\beta\alpha\gamma\delta} \end{aligned} \quad (7.52)$$

From cylindrical symmetry, the x-components of properties are indistinguishable from the y-components. Moreover, there is no way to distinguish  $\underline{n}$  from  $-\underline{n}$ . The free energy can be written

$$F = \frac{1}{2} K_1 (\underline{\nabla} \cdot \underline{n})^2 + \frac{1}{2} K_2 (\underline{n} \cdot \underline{\nabla} \times \underline{n})^2 + \frac{1}{2} K_3 (\underline{n} \times (\underline{\nabla} \times \underline{n}))^2 \quad (7.53)$$

$$K_1 = \frac{1}{2} \bar{c}_{xxxx} \quad (7.54a)$$

$$K_2 = \frac{1}{2} \bar{c}_{xxyy} \quad (7.54b)$$

$$K_3 = \frac{1}{2} \bar{c}_{zzxx} \quad (7.54c)$$

where  $K_i$  are the Frank elastic constants. These are the expressions obtained by Stecki et al [10]. They used the Onsager approximation to calculate  $K_i$ . In Appendix 7.2, the expressions (7.54) are related to the quantities

$$c''_{\pm 1 \pm 1}{}^{mn0}(0), c_{\pm 1 \pm 1}{}^{mn2}(0)$$

where

$$c''_{\mu\nu}{}^{mn1}(0) = \int_0^\infty dr r^4 c_{\mu\nu}{}^{mn1}(r) \quad (7.55)$$

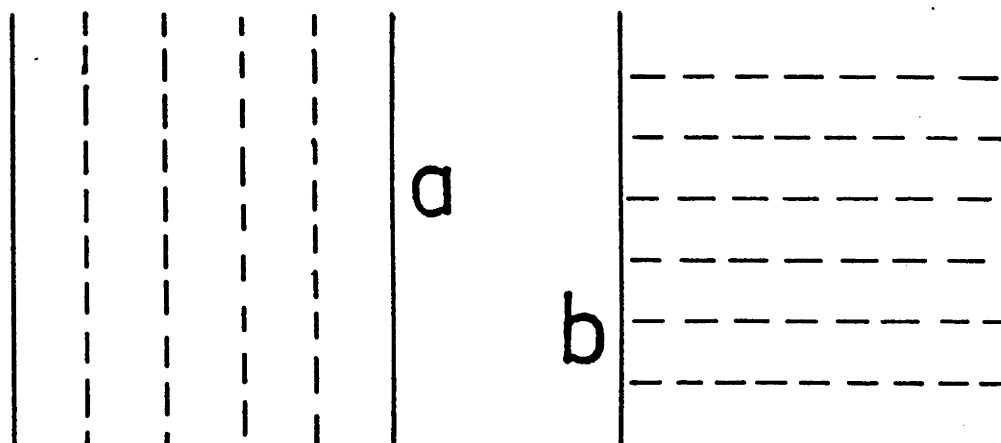
7.9 Alignment of liquid crystals at a wall

Fig. 7.4

At a liquid crystal solid interface, the solid substrate can have considerable influence on the properties of the director of the liquid crystal. For instance, the surface can be treated so the director is perpendicular to the surface (homeotropic orientation). In the situation illustrated in Fig. 7.4(a) and (b) where a nematic liquid crystal is sandwiched between the two surfaces the director is not distorted and there is no elastic energy associated with such distributions. Nevertheless, the surfaces can still affect the ordering molecules so that the order parameter at the surface is different from that in bulk. This has led to birefringence studies of liquid crystals at prepared surfaces [11]. The purpose of this section is to investigate whether this ordering can lead to forces between the surfaces for the situation illustrated in Fig. 7.4(a) and (b).

Let  $x$  denote the distance from one wall.

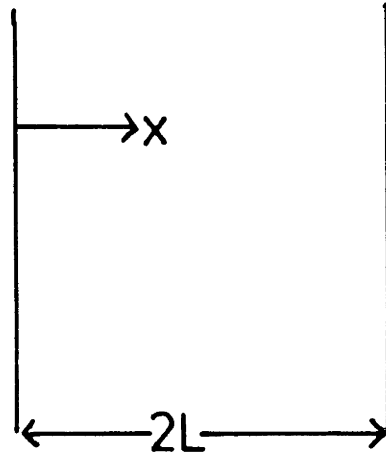


Fig. 7.5

The difference in free energy between the volume of liquid crystal between the surfaces and that of the same volume of bulk liquid crystal is given by (6.24)

$$\begin{aligned} \frac{\beta \Delta \Omega}{A} &= \int_0^{2L} dx \int d\omega_1 \rho(x, \omega_1) \ln \left( \frac{\rho(x, \omega_1)}{\rho_0(\omega_1)} \right) \\ &+ (\rho(x, \omega_1) - \rho_0(\omega_1)) - \frac{1}{2} \int_0^{2L} dx \int_0^{2L} dx' \\ &\quad \bar{c}(r, \omega_1, \omega_2, r) (\rho(x, \omega_1) - \rho_0(\omega_1)) \\ &\quad (\rho(x, \omega_2) - \rho_0(\omega_1)) + F_S \end{aligned}$$

where  $\frac{\Delta \Omega}{A}$  is the change of free energy per unit area,  $2L$  is the separation of the walls,  $\rho_0$  is the density distribution of the bulk nematic phase and  $F_S$  is the free energy due to the liquid crystal. For very small separations there will be forces due to the packing of particles (Section 6.5). However at large distances from the wall, it is expected that the order parameter is changing without significant change to the density. Suppose for large separations, the free energy is only dependent on the order parameter  $S_2(x)$ . Then the change in

free energy is given by

$$\begin{aligned} \Delta \frac{(\beta\Omega)}{A} &= \int_0^{2L} dx \int_{\omega_1} d\omega \rho(x, \omega_1) \ln \left( \frac{\rho(x, \omega_1)}{\rho_0(\omega_1)} \right) \\ &\quad - \frac{1}{2} \int_0^{2L} dx \int_0^{2L} dx' \bar{c}_{oo}^{220}(x-x') (S_2(x) - S_{\text{bulk}}) (S_2(x') - S_{\text{bulk}}) \\ &\quad + F_S \end{aligned} \quad (7.57)$$

Here,

$$\begin{aligned} \bar{c}_{oo}^{220}(x-x') &= \frac{1}{4\pi^2} \int_0^\pi d\phi \int_0^\pi d\phi' \int_0^\infty dr r^2 \\ &\quad \int_0^1 P_2(\cos\theta') d(\cos\theta') \int_0^1 d(\cos\theta) P_2(\cos\theta) c(1,2) \end{aligned} \quad (7.58)$$

where the Euler angles of  $\omega_1, \omega_2$  are  $(\phi, \theta, \chi)$  and  $(\phi', \theta', \chi')$  respectively.

The term  $S_{\text{bulk}}$  is the bulk value of the order parameter. If the bulk phase is isotropic,  $S_{\text{bulk}}$  is zero. The second term can be expanded using the Landau approximation (section 6.5) to give

$$\int_0^{2L} dx \left[ \frac{1}{2} U \beta (S(x) - S_0)^2 + \xi_0^2 \left( \frac{dS}{dx} \right)^2 \right] \quad (7.59a)$$

$$U = -kT \int_0^\infty dx \bar{c}_{oo}^{220}(x) \quad (7.59b)$$

$$\xi_0^2 = 2 \int_0^\infty dx \bar{c}_{oo}^{220}(x) x^2 \quad (7.59c)$$

It is assumed hereafter that  $U$  and  $V$  are independent of the second

order parameter  $S$ . We adopt the attitude of Akahane and Tako [12] in approximating

$$\int_0^{2L} dx \int d\omega_1 \rho(x, \omega_1) \ln \left( \frac{\rho(x, \omega_1)}{\rho_0(\omega_1)} \right) \quad (7.60)$$

by the Maier-Saupe Approximation

$$\int_0^{2L} dx \left[ \beta U(S - S_{\text{bulk}})^2 - \log \int_0^1 dy \exp(-\beta U S^2(y)) \right] \quad (7.61)$$

The change in free energy can then be written

$$\Delta \left( \frac{\beta \Omega}{A} \right) = \left[ \int_0^{2L} dx (F(S(x)) - F(S_0)) + \xi_0^2 \left( \frac{dS}{dx} \right)^2 \right] + F_S \quad (7.62)$$

$$F(S(x)) \approx F(S_0) + \frac{1}{2} F''(S_0) (S - S_0)^2 \quad (7.62)$$

where  $F(S)$  is the Maier-Saupe expression for the free energy of a bulk system in which the second order parameter is  $S$ .

The expression (7.62) is minimised by the second order parameter  $S(x)$  where

$$\frac{d^2 S}{dx^2}(x) = \frac{F''(S_{\text{bulk}})}{2(\xi_0)^2} (S - S_{\text{bulk}}) \quad .$$

One boundary condition is the symmetry condition

$$\frac{dS}{dx}(L) = 0$$

Equation (7.64) has the solution

$$S(x) = S_o + \frac{(S_b - S_{bulk}) \cosh\left(\left(\frac{L-Z}{\xi_o}\right) \frac{\sqrt{F''(S_{bulk})}}{2}\right)}{\cosh\left(\frac{\sqrt{F''(S_o)}}{2} \frac{L}{\xi_o}\right)} \quad (7.66)$$

where

$$S_b = S_2(0) \quad (7.67)$$

is determined by the surface free energy term  $F_S$ . For  $S_o = .5$  the scale length is

$$\left(\frac{2}{F''(S_{bulk})}\right)^{\frac{1}{2}} \xi_o \approx 6\xi_o \quad (7.68)$$

Near the transition temperature it is expected [7] that  $\xi_o$  is of the form

$$\xi_o(T) = \frac{\xi_o(T_c)}{|T - T_c|} \quad (7.69)$$

where  $\xi_o(T_c)$  is  $0(100 \text{ \AA})$ .

If  $F_S$  only depends on  $S_b$  and  $\frac{dS_b}{dx} \left( \equiv \frac{dS}{dx}(0) \right)$  the expression (7.62) is of the same form as (6.35) and hence from (6.68) the pressure is given by

$$\begin{aligned} p &= \frac{1}{A} \frac{\partial(\Delta\Omega)}{\partial(2L)} = \int_{S_o}^{S_b - S_{bulk}} dS_b \left( \frac{dS_b}{dx} \right) (\text{separation} = 2L) \\ &\quad - \frac{dS_b}{dx} (\text{separation} = \infty) \\ &= -4\xi_o (S_b - S_{bulk}) \frac{\sqrt{F''(S_{bulk})}}{2} e^{-2 \frac{\sqrt{F''(S_{bulk})}}{2} \frac{d}{\xi_o}} \end{aligned} \quad (7.70)$$



As the temperature falls the scale length (7.68) becomes smaller and the separation at which the force is significant decreases.

Near  $T_c$ ,  $F''(S_o)$  becomes very small and further terms in the Taylor expansion are needed i.e.

$$F(S) \approx F(S_{bulk}) + \frac{F''(S_{bulk})}{2} (S - S_{bulk})^2 + \frac{F'''(S_{bulk})}{6} (S - S_{bulk})^3 + \frac{F^{(iv)}(S_{bulk})}{24} (S - S_{bulk})^4 \quad (7.71)$$

This is equivalent to the Landau - de Gennes expansion (7.39) with

$$a(T - T_o) = F''(S_{bulk}) \quad (7.72a)$$

$$b = \frac{F''(S_{bulk})}{2} \quad (7.72b)$$

$$c = \frac{F^{(iv)}(S_{bulk})}{6} \quad (7.72c)$$

The expression (7.62) becomes

$$\beta\left(\frac{\Delta\Omega}{A}\right) = \int_0^{2L} dx \left( a \frac{(T - T_o)}{2} (S - S_{bulk})^2 - b \frac{(S - S_{bulk})^3}{3} + c \frac{(S - S_{bulk})^4}{4} + \xi_o^2 \left( \frac{dS}{dx} \right)^2 \right) \quad (7.73)$$

This is minimised by

$$2\xi_o^2 \frac{d^2 S}{dx^2} = -a(T - T_o) (S - S_{bulk}) + b(S - S_{bulk})^2 - c(S - S_{bulk})^3 \quad (7.74)$$

with the boundary condition

$$\frac{dS}{dx}(L) = 0 \quad . \quad (7.75)$$

Eqn. (7.74) cannot be solved exactly for finite  $L$ . For the single wall, the solution is given in reference [3]. At a large distance  $x$  from the wall this is given by

$$S - S_{\text{bulk}} = f(S_b) \exp(-\xi_0 x / \sqrt{a(T - T_0)}) \quad (7.76)$$

where  $f(S_b)$  diverges as  $T \rightarrow T_c$ . The scale length

$$\frac{\sqrt{a(T - T_0)}}{\xi_0} \quad (7.77)$$

also goes to infinity. If the bulk phase is isotropic the order parameter goes to zero. However, the scale length over which significant changes in order parameter occur goes to infinity as  $T \rightarrow T_c$ .

One can speculate about the behaviour of the liquid crystals between two walls. If the separation,  $2L$ , is very large, the so-called 'overlap' approximation can be used i.e. the order parameter  $S(x)$  is given by

$$S(x) = S_{\text{single wall}}(x) + S_{\text{single wall}}(2L - x) \quad (7.78)$$

where  $S_{\text{single wall}}(x)$  is the order parameter at  $x$  for the single

wall. For this, the separation  $2L$  must be greater than the scale length. For temperatures just greater than  $T_c$ , there is a possibility of a surface induced transition as the separation is decreased i.e. the order parameter  $S(x)$  is given by

$$S(x) = S_{\text{metastable}}(x) + S_{\text{metastable}}(2L - x) \quad (7.79)$$

where  $S_{\text{metastable}}(x)$  is the order parameter at  $x$  for single wall if the order parameter went to  $S_c$  and not zero as  $x$  approaches infinity. The form of  $S_{\text{metastable}}(x)$  is given in [3]. This is a possible area for future research.

#### 7.10 Discussion

In this chapter a framework for discussing the properties of liquid crystals has been established. In deriving the free energy expression for a liquid crystal the molecular properties are linked to the macroscopic properties by the direct correlation function. The effect of molecular properties on the general form of the direct correlation function was discussed in section 7.2. However a knowledge of the correlation function is needed to calculate the free energy. For discussing the isotropic-nematic transition this correlation function is needed at each stage of the process. Unfortunately such information is not readily available.

However it was shown in section 7.5 that the similarity in the local structure in isotropic and nematic phases allows the calculation of the direct correlation function at all stages of the

process by simply knowing certain details of the isotropic phase. Such details would include the arrangement of particles in a small volume about any given particle, and could be obtained by computer simulations or numeric studies . Once this is done, then the theory could be tested by comparing the parameters (7.28) as obtained by this theory and those needed to fit experiment. It could also test whether terms such as  $V_2$  (7.29) which are not normally included in mean field theories are significant.

In the final sections, non-uniform systems were discussed. The elastic constant  $K_i$  were written in terms of the terms

$$\int_0^{\infty} c_{\mu\nu}^{mnl}(r) r^2 dr$$

and

$$\int_0^{\infty} c_{\mu\nu}^{mnl}(r) r^4 dr.$$

If the correlation functions are known, then  $K_i$ ,  $i = 1,2,3$ , can be calculated. Finally the pressure has been calculated for the system in which two walls are separated by a liquid crystal. This raises the possibility of a surface - induced transition.

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### Appendix 7.1      Direct correlation function

Suppose at a particular time the direct correlation function at  $\underline{S}$  is given by

$$c_{loc}(\underline{r}, \underline{\omega}_1, \underline{\omega}_2, \underline{\omega}_n) = \sum_{\substack{m,n,\ell \\ \mu,\nu}} c_{\mu\nu}^{mn\ell}(\underline{r}) D_{o\mu}^{*M}(\underline{\omega}_1) D_{o\nu}^n(\underline{\omega}_2) D_{o\lambda}^\ell(\hat{\underline{r}}) \delta_{\lambda, \mu-\nu} \quad (A.1)$$

where the orientations are measured w.r.t. to the local nematic axis. Rewriting these orientations in terms of the bulk director yields

$$c_{loc}(\underline{r}, \underline{\omega}_1, \underline{\omega}_2, \underline{\omega}_n) = \sum_{\substack{mn\ell \\ \mu,\nu}} c_{\mu\nu,loc}^{mn\ell}(\underline{r}) (-)^{\mu} \sum_{\mu',\nu',\lambda'} D_{o\mu'}^m(\underline{\omega}_1') D_{o\nu'}^n(\underline{\omega}_2') D_{o\lambda'}^\ell(\hat{\underline{r}}') \delta_{\lambda, \mu-\nu} \\ \times D_{\mu',-\mu}^m(\hat{\underline{Z}}) D_{\nu',\nu}^n(\hat{\underline{Z}}) D_{\lambda',\lambda}^\ell(\hat{\underline{Z}}) \quad (A.2)$$

where  $\underline{\omega}_1'$ ,  $\underline{\omega}_2'$ ,  $\hat{\underline{r}}'$  are the same orientation as in (A.1) except that they are measured with respect to the bulk director. The orientation of the bulk director w.r.t. the local director at  $\underline{r}$  and  $\underline{Z}$ . The probability that at  $\underline{S}$  the local director makes an angle between  $\theta$  and  $\theta + d\theta$  with respect to the bulk director is given by

$$h(\theta) d(\theta) \quad (A.3)$$

The bulk direct correlation function is given by

$$c(\underline{r}, \underline{\omega}_1, \underline{\omega}_2, \hat{z}) = \int_0^\pi d\theta h(\theta) c(\underline{r}, \underline{\omega}_1, \underline{\omega}_2, \underline{\omega}_n) \quad (\text{A.4})$$

For the isotropic phase

$$h(\theta) = 1 \quad (\text{A.5})$$

and (A.4) reduces to

$$c(\underline{r}, \underline{\omega}_1, \underline{\omega}_2) = \sum_{mn\ell} \sum_{\mu'v'\lambda'} c_{\mu v, loc}^{mn\ell}(\underline{r}) (-)^{\mu+\mu'}$$

$$D_{o-\mu}^{m*}(\underline{\omega}_1) D_{ov}^n(\underline{\omega}_2) D_{o\lambda}^\ell(\hat{z}) \delta_{\lambda, \mu-v}$$

$$\int d\hat{z} D_{\mu, -\mu}^m(\hat{z}) D_{v, v}^n(\hat{z}) D_{\lambda, \lambda}^\ell(\hat{z}) \quad (\text{A.6})$$

$$= \sum_{mn\ell} \sum_{\mu, v} c_{\mu v, loc}^{mn\ell}(\underline{r}) (-)^{\mu+\mu'} D_{o-\mu}^n(\underline{\omega}_1)$$

(A.7)

$$D_{ov}^n(\underline{\omega}_1) D_{o\lambda}^\ell(\hat{z}) \begin{pmatrix} m & n & \ell \\ \mu & v & \lambda \end{pmatrix} \begin{pmatrix} m & n & \ell \\ -\mu & v & \lambda \end{pmatrix} \delta_{\lambda, \mu-v}$$

$$= \sum_{mn\ell} \sum_{\mu, v} c_{\mu v, loc}^{mn\ell}(\underline{r}) \begin{pmatrix} m & n & \ell \\ +\mu & -v & -\lambda \end{pmatrix} (-)^\mu \phi_{oo}^{mn\ell}(\underline{\omega}_1, \underline{\omega}_2, \hat{z}) \quad (\text{A.8})$$

Therefore in the isotropic phase the coefficients  $c_{oo}^{mn\ell}(r)$  are given by

$$c_{oo}^{mn\ell}(r) = \sum_{\mu, \nu} c_{\mu\nu, loc}^{mn\ell}(r) \begin{pmatrix} m & n & \ell \\ \mu & -\nu & -\lambda \end{pmatrix} (-)^{\mu} \quad (A.9)$$

The coefficients  $c_{oo}^{mn\ell}$  will from now be denoted  $c_{iso}^{mn\ell}$ . For the nematic phase

$$h(\theta) = \left( 1 + \sum_{L=2}^{\infty} h_L P_L(\cos \theta) \right) \quad (A.10)$$

and the direct correlation function is given by

$$c(\underline{r}, \omega_1, \omega_2, \hat{z}) = \sum_{mn\ell} \sum_{\mu, \nu, \lambda'} c_{\mu\nu, loc}^{mn\ell}(r)$$

$$(-)^{\mu+\mu'} D_{o-\mu}^m(\omega_1) D_{o\nu}^n(\omega_2) D_{o\lambda}^{\ell}(\hat{r}) \delta_{\lambda, \mu-\nu}$$

$$\sum_L \int a \hat{z} h_L D_{\mu, -\mu}^m(\hat{z}) D_{\nu, \nu}^n(\hat{z}) D_{\lambda, \lambda}^{\ell}(\hat{z}) D_{oo}^L(\hat{z})$$

$$= \sum_{mn\ell} \sum_{\mu, \nu, \lambda'} \sum_L c_{\mu\nu, loc}^{mn\ell}(r) h_L (-)^{\mu+\mu'+\lambda'+\lambda}$$

$$\sum_P \begin{pmatrix} \ell & L & P \\ \lambda' & 0 & -\lambda' \end{pmatrix} \begin{pmatrix} \ell & L & P \\ \lambda & 0 & -\lambda \end{pmatrix} \delta_{\lambda, \mu-\nu} \begin{pmatrix} m & n & P \\ \mu & \nu & \lambda' \end{pmatrix}$$



$$\begin{aligned}
& \begin{pmatrix} m & n & P \\ -\mu & v & \lambda \end{pmatrix} D_{o-\mu}^m(\omega_1) D_{ov}^n(\omega_2) D_{o\lambda}^\ell(\hat{r}) \\
&= \sum_{mn\ell} \left[ c_{iso}^{mn\ell}(r) \phi_{oo}^{mn\ell}(\omega_1, \omega_1, \hat{r}) \right. \\
&+ \left. \sum c_{-\mu', v', nem}^{mn\ell}(r) \psi_{-\mu', v'}^{mn\ell}(\omega_1, \omega_2, \hat{r}, \hat{z}) \right]
\end{aligned}$$

where

$$c_{-\mu', v', nem}^{mn\ell}(r) = \sum_{\mu, v} c_{\mu v, loc}^{mn\ell}(r) \sum_{L=2}^{\infty} h_L$$

$$(-)^{\mu+\mu'+\lambda'+\lambda} \sum_P \begin{pmatrix} \ell & L & P \\ \lambda' & 0 & -\lambda' \end{pmatrix} \begin{pmatrix} \ell & L & P \\ \lambda & 0 & -\lambda \end{pmatrix}$$

(A.11)

$$\delta_{\lambda, \mu-v} \begin{pmatrix} m & n & P \\ \mu' & v' & \lambda' \end{pmatrix} \begin{pmatrix} m & n & P \\ -\mu & v & \lambda \end{pmatrix}$$

Of particular interest is the term

$$c_{oo, nem}^{220} = c_{iso}^{220} + \sum_{\mu} c_{\mu\mu, 25}^{220} \frac{h_2}{5} (-)^{\mu} \begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix}$$

(A.12)

$$\begin{pmatrix} 2 & 2 & 2 \\ \mu & -\mu & 0 \end{pmatrix} + \sum_{L=4}^{\infty} (\dots) \quad .$$

## Appendix 7.2 Elastic Constants

There are a number of results that need to be known before  $K_1$  can be calculated

$$\begin{aligned}
(i) \quad \omega_x^1 \rho'(\cos \theta) &= \sin \theta \cos \phi \sum_L \rho_0 (2L+1) S_L P'_L(\cos \theta) \\
&= \rho_0 \sum_L \frac{S_L}{2} (P_L^1(\cos \theta) (e^{i\phi} + e^{-i\phi}) (2L+1))
\end{aligned}$$

$$\begin{aligned}
&= \rho_0 \sum_L \frac{S_L}{2} (P_L^1(\cos \theta) e^{i\phi} + P_L^{-1} e^{-i\phi}) (2L + 1) \\
&= \rho_0 \sum_L \frac{S_L}{2} ((L + 1)L)^{1/2} (D_{01}^L(\hat{\omega}_1) + D_{0-1}^L(\hat{\omega}_1)) (2L + 1) \quad (\text{B.1})
\end{aligned}$$

$$\begin{aligned}
(ii) \quad r_x^2 &= r^2 \sin^2 \theta_r \cos^2 \phi_r \\
r_y^2 &= r^2 \sin^2 \theta_r \sin^2 \phi_r \\
r_z^2 &= r^2 \cos^2 \theta_r
\end{aligned}$$

$$r_x^2 - r_y^2 = r^2 \sin^2 \theta_r \cos 2\phi_r = \frac{r^2}{6} (D_{02}^2(\hat{\mathbf{r}}) + D_{0-2}^2(\hat{\mathbf{r}})) \quad (\text{B.2})$$

$$\frac{(r_x^2 + r_y^2 + r_z^2)}{3} = \frac{r^2}{3} = \frac{r^2}{3} D_{00}^0 \quad (\text{B.3})$$

$$\frac{(2r_z^2 - r_x^2 - r_y^2)}{2} = r^2 \left( \frac{3}{2} \cos^2 \theta_r - \frac{1}{2} \right) = r^2 D_{00}^2(\hat{\mathbf{r}}) \quad (\text{B.4})$$

$$K_1 = \frac{1}{12} \sum_L \sum_{L'} \frac{S_L S_{L'}}{3} (L(L+1)L'(L'+1))^{1/2} (2L+1)(2L'+1)$$

$$\times \left( -\hat{c}_{-1-1}^{LL'0}(0) - \hat{c}_{11}^{LL'0}(0) + \hat{c}_{-1-1}^{LL'2}(0) \right)$$

$$+ \hat{c}_{11}^{\prime\prime LL'2}(0) - \frac{1}{4} \hat{c}_{-11}^{\prime\prime LL'2}(0) - \frac{1}{4} \hat{c}_{1-1}^{\prime\prime LL'2}(0) ) \quad (\text{B.5})$$

$$\begin{aligned} K_2 &= \frac{1}{12} \sum_L \sum_{L'} S_L S_{L'} \left( L(L+1)L'(L'+1) \right)^{1/2} (2L+1) \\ &\times (2L'+1) \left( -\hat{c}_{-1-1}^{\prime\prime LL'0}(0) - \hat{c}_{11}^{\prime\prime LL'0}(0) + \hat{c}_{-1-1}^{\prime\prime LL'2}(0) \right. \\ &\left. + \hat{c}_{11}^{\prime\prime LL'2}(0) + \frac{1}{4} \hat{c}_{-1-1}^{\prime\prime LL'2}(0) + \frac{1}{4} \hat{c}_{1-1}^{\prime\prime LL'2}(0) \right) \quad (\text{B.6}) \end{aligned}$$

$$\begin{aligned} K_3 &= \frac{1}{12} \sum_L \sum_{L'} S_L S_{L'} \left( L(L+1)L'(L'+1) \right)^{1/2} (2L+1) \\ &\times (2L+1) \left( -\hat{c}_{-1-1}^{\prime\prime LL'0}(0) - \hat{c}_{1-1}^{\prime\prime LL'0}(0) + 2 \hat{c}_{-1-1}^{\prime\prime LL'2}(0) \right. \\ &\left. + 2 \hat{c}_{1-1}^{\prime\prime LL'2}(0) \right) \quad (\text{B.7}) \end{aligned}$$

$$\hat{c}_{\mu\nu}^{\prime\prime mn\ell}(0) = \int_0^\infty dr \, r^4 c_{\mu\nu}^{\prime\prime mn\ell}(r) \quad (\text{B.8})$$