# New aspects in the simulation and behaviour of
# polar molecular fluids

by E. LOMBA and M. LOMBARDERO

Instituto de Química Física Rocasolano, C.S.I.C.
Serrano 119, E-28006 Madrid, Spain,
and Depto. Química Física, Facultad de CC. Químicas,
Universidad Complutense de Madrid,
E-28040 Madrid, Spain

and J. L. F. ABASCAL

Depto. Química Fisica, Facultad de CC. Químicas,
Universidad Complutense de Madrid,
E-28040 Madrid, Spain

A Monte Carlo computer simulation study of a simple model for dipolar molecular fluids is reported. Long-range interactions are treated by the Reaction Field method. A detailed investigation of the density dependence of dielectric, structural and thermodynamic properties is presented. At moderately high densities the dielectric constant is found to exhibit a clear maximum. Special attention has also been addressed to the influence of sample size and cutoff radius on dielectric properties; unlike the case of dipolar hard sphere fluids, such properties are rather sensitive to changes in the sample size, whereas the cutoff radius seemingly plays a minor role.

## 1. Introduction

In the last decade a significant number of computer simulation studies on dipolar fluids have appeared [1–8, 10–11]. These works have helped to clarify a rather confusing situation in relation to the influence of boundary conditions and sample size on the results, especially on the dielectric constant. Most of the studies are concerned mainly with models of spherically shaped particles in which the electrostatic interactions are included as point multipoles [5, 8] or separated charges [12]; even though the reproducibility of the results for this system does not seem to have reached a completely satisfactory stage, we consider that a consensus is emerging. The situation is not the same for molecular fluids. Some studies on diatomic dipolar fluids (both homonuclear [9, 10] and heteronuclear [11]) and even on more complicated systems (such as a three-centre Lennard-Jones with point charges model for $CH_3$–$C{\equiv}N$ [3]) have been carried out; but in practice these questions are far from being definitely settled.

The motivation of this present work is the calculation of the dielectric constant of molecular fluids (and its density dependence) in order to check the predictions of integral equation theories. The model considered by us is the dipolar homonuclear hard diatomic, i.e. a system of two fused hard spheres of equal size with an embedded point dipole located at the centre of the molecule. A similar model has been

previously investigated by Morris and Cummings [9] and Morriss [10] who used a 'real' dipole (two point charges of opposite sign located in the atomic sites). The hamiltonian functions corresponding to each of these systems are rather different but one may expect that the point dipole term (the first and leading term of the multiple expansion) should contain the most significant features of the 'real' dipole system. The advantage of the former model lies in the fact that point dipoles can be dealt with more simply in the framework of molecular based integral equation theories (i.e. theories not based on a site–site approach) [13, 14]. In this context the reaction field (RF) method is suitable for the treatment of long range forces since it enables a definite comparison between theory and simulation provided that both are carried out in a consistent way [6]. The use of point charge dipoles introduces some severe problems in the implementation of the RF method, particularly in the computation of the reaction field [8].

In the course of our work several new problems arose indicating that a more detailed study was needed. In particular, the influence of the boundary conditions and sample size on the properties of the diatomic dipolar fluid is significantly different from that exhibited by the dipolar hard sphere system. The same holds for the density dependence of the dielectric constant. Thus, the final motivation of this paper is to gain some knowledge of the dielectric behaviour of model molecular systems, which could help in our understanding of real molecular fluids.

We have devoted §2 to the main features of the RF methodology. In §3 the structural properties (coefficients of the expansion of the pair distribution function in rotational invariants) are presented. A comparison between the results obtained for the point dipole and the 'real' dipole [9] models is included. Section 4 describes the influence of the cutoff radius and the sample size on the simulation results. Finally, in §5 we deal with the macroscopic dielectric and thermodynamic properties of the dipolar fluid. Special attention is paid to the density dependence of the dielectric constant. From our research it becomes clear that the shape forces are the main reason for the low values of the dielectric constant in most attempts to model real liquids [15] and that the effect of quadrupolar interactions, even though not negligible, is a secondary factor.

## 2.  Some theoretical remarks

The long-range interactions between dipolar molecules can be tackled by two different approaches, namely the Ewald summation technique (see, e.g., [1]) and the Reaction Field method [16]. The first of these approaches is based on the assumption of the periodicity of the sample and it yields results for a model with an infinite-range (non-truncated) potential. Its main disadvantage lies in the fact that it is very time consuming. Besides, the use of the RF enables a more immediate and precise comparison between simulation and theoretical results. The RF method uses a truncated potential in which the effects of the long range dipolar interactions are corrected by surrounding the truncation sphere with a polarizable dielectric continuum. Actually, this implies that the system energy is given by

$$U = \sum_{i<j} u(ij)\, H(R_c - r_{ij}) - \frac{1}{2} \sum_i \mathbf{R}_i \cdot \boldsymbol{\mu}_i \tag{1}$$

where $H(x)$ is a step function, $u(ij)$ is the dipole–dipole interaction, $R_c$ is the cutoff radius of the interaction, and $\mathbf{R}_i$ is the reaction field acting on particle $i$ due to the

polarization of the continuum, namely

$$\mathbf{R}_i = \frac{2(\varepsilon' - 1)}{2\varepsilon' + 1} (\mathbf{M}_i)_{\text{sph}}/R_c^3 \qquad (2)$$

$(\mathbf{M}_i)_{\text{sph}}$ being the total dipolar moment of the truncation sphere. The $\varepsilon'$ is the dielectric constant of the continuum. It can be shown that the total energy is the same as that of a system of $N$ particles interacting pairwise according to an effective potential

$$u_{\text{RF}}(12) = \begin{cases} u(12) - \dfrac{2(\varepsilon' - 1)}{2\varepsilon' + 1} \mu^2 \, \Phi^{110}(12)/R_c, & \text{if} \quad r < R_c, \\ 0, & \text{if} \quad r \geqslant R_c, \end{cases} \qquad (3)$$

in which $u(12) = -\mu^2 \Phi^{112}(12)/r^3$. In these expressions $\Phi^{110}(12) = \mathbf{s}_1 \cdot \mathbf{s}_2$ and $\Phi^{112} = 3(\mathbf{s}_1 \cdot \mathbf{r})(\mathbf{s}_2 \cdot \mathbf{r})/r^2 - (\mathbf{s}_1 \cdot \mathbf{s}_2)$ are rotational invariants, and $\mathbf{s}_i$ is a unit vector which describes the orientation of particle $i$.

As it has been proven in previous works [2], the use of the reaction field implies that the correct dipole moment fluctuation formula is

$$\frac{(\varepsilon - 1)(2\varepsilon' + 1)}{3(\varepsilon + 2\varepsilon')} = y\langle M^2 \rangle/N\mu^2 \qquad (4)$$

and

$$g_k = \langle M^2 \rangle/N\mu^2 = 1 + \frac{\rho}{3} \lim_{R_c \to \infty} \tilde{h}^{110}(0; R_c) \approx 1 + \frac{\rho}{3} \tilde{h}^{110}(0; R_c) \qquad (5)$$

where the tilde denotes a 3-D Fourier transform and the $h^{110}(r)$ is one of the coefficients of the total correlation function $h(12)$ expansion in rotational invariants. The $R_c$ in equation (5) means that the function $h(12)$ corresponds to a system which interacts via the effective potential described by equation (3). The approximation above stated is only valid if the sample size is sufficiently large [6]. As has been stressed by Patey *et al.* [6] the $\langle M^2 \rangle$ must be calculated in the cubic simulation cell and not in the truncation sphere.

From the above expressions the RF–MC simulation of a dipolar hard diatomic fluid can be handled without further difficulties, provided that appropriate values of $R_c$ and $\varepsilon'$ have been set.

## 3. The microscopic structure

Following previous works [9, 10], we consider the dipolar hard diatomic fluid to be the simplest model that can account for the effects of the molecular anisotropy as far as the structure and dielectric properties are concerned. As already mentioned, our model consists of two fused hard spheres whose centres are separated by a distance $l = 0.6\sigma$ ($\sigma$ being the hard sphere diameter). The quantity $y = 4\pi\rho\mu^2/(9kT)$ is set to 1.49 and $\rho d^3 = 0.78$ ($d^3 = \sigma^3 + \frac{3}{2}l\sigma^2 - \frac{1}{2}l^3$ is the cubed diameter of a sphere of the same volume as the diatomic). This choice enables a comparison with the point charge model of [9, 10]. Such model may represent liquid $CH_3Cl$ at room temperature.

If the RF method is used, some more parameters are required to wholly determine the system, namely the cutoff radius, $R_c$, and the continuum dielectric constant, $\varepsilon'$. In this work we use two different values of $R_c$, namely $4\sigma$ and $5\sigma$. The

latter has only been used to check the influence of this parameter on the final results. As we shall see in §4 this influence turned out to be negligible. As to the value of $\varepsilon'$, our choice was that proposed by Patey *et al.* [6] for polar hard spheres so as to reproduce the value of $\varepsilon$ corresponding to a system with untruncated potential. In fact, previous works on the RF method [17] indicate that different choices of $\varepsilon'$ should yield the same value of $\varepsilon$ if equation (4) is used to compute this quantity.

In order to analyse the orientational structure and its density dependence, the coefficient $h^{110}(r)$

$$h^{110}(r) = 3\langle \cos \theta_{12}(r) \rangle \tag{6}$$

is of special interest. In equation (6), $\theta_{12}(r)$ is the angle between the axes of two particles separated by a distance $r$. Since $h^{110}(r)$ is zero for the hard diatomics system, it describes the additional ordering induced in the sample by the dipolar interaction.

Two series of simulations have been performed. At the lower densities $\rho\sigma^3 = 0.2$, 0.3 and 0.4352 (which, for $l/\sigma = 0.6$, corresponds to $\rho d^3 = 0.78$) 256 and 500 particle samples were used and at the highest density $\rho\sigma^3 = 0.5$, the sample contained 500 molecules. In both series the cutoff distance has been set to $R_c = 4\sigma$. An additional point at $\rho\sigma^3 = 0.4352$ using $R_c = 5\sigma$ and 500 particles has also been computed in order to analyse the influence of the cutoff radius on the dielectric properties. Over 1.5 million configurations were generated to allow the system to attain the thermal equilibrium. The production step ranged from 5 to 7.5 million configurations with average performed every 1500 moves.

Our results confirm previous conclusions, stated for different models of linear molecules [3, 10], in that the molecular anisotropy is the leading factor in determining the orientational structure. The introduction of the dipole is hardly noticeable in the coefficients with even indexes and the behaviour of $h^{110}$ and $h^{112}$, which are solely due to the symmetry breaking effects of the dipolar interaction, is determined by molecular shape. In fact, our computed $h^{110}(r)$ and $h^{112}(r)$ coefficients, presented in figure 1, and those obtained when one uses point charge models [9] or three centre Lennard-Jones plus point charges [3], are quite alike. Conversely, if a spherical model is considered, the coefficients are strikingly different (see, e.g., [6, 7]).

It is well known, and can be easily derived from (6), that negative values of $h^{110}$ are associated with dipoles aligned antiparallel. Subsequently, an orientational structure in two layers may be observed: the first one, located at $r \lesssim \sigma$, is antiparallel while the second one is parallel, and is located at $r \simeq 1.5\,\sigma$. The effect of increasing density on the orientational order is shown in figure 1. Both maxima and minima are enhanced as the density is increased which, from (6), implies larger values of $|\langle \cos \theta_{12} \rangle|$. Another effect stemming from the rise in density is the shift in the position of maxima and minima towards lower values of $r$. This is associated to a compression of the system, which tends to occupy the minimum volume as density increases. The positions of the extrema are compatible with a molecular ordering as indicated in the right upper corner of figure 1 (*a*). This explains why these values differ from those found for polar hard spheres, where the maxima are located at $\sigma$, $2\sigma$, etc. ... [6].

Another function entirely due to the dipolar interaction is $h^{112}(r)$. In order to get some physical insight from figure 1 (*b*), where this coefficient is shown for several densities, one must recall that $h^{112}$ is related to the average dipole–dipole inter-
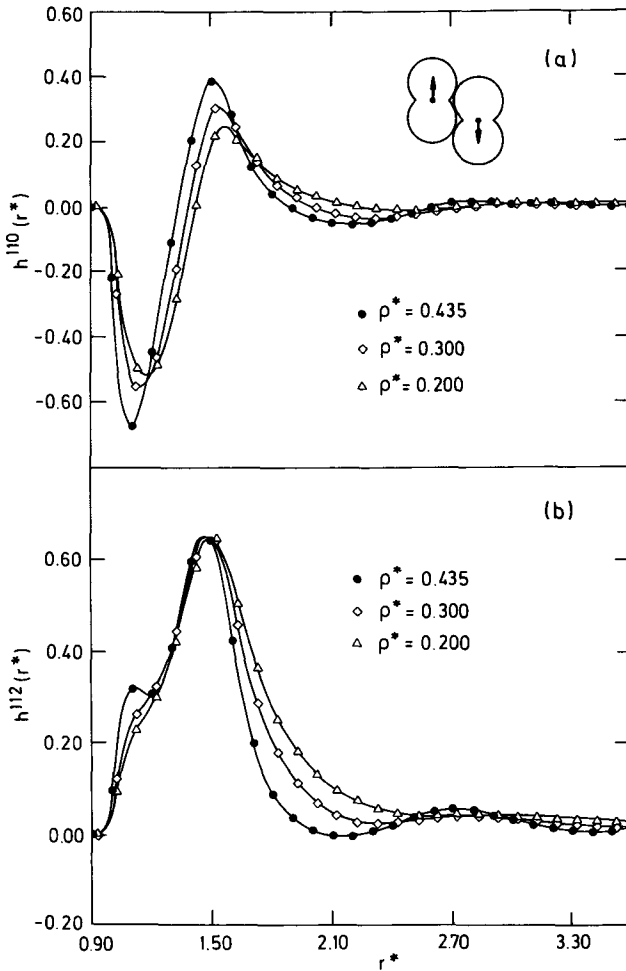
Figure 1. Coefficients $h^{110}(r)$ (a) and $h^{112}(r)$ (b) computed at several densities with $R_c = 4\sigma$. Lines are drawn as a guide to the eye.

action for a given centre-to-centre separation

$$u_{av}(r) = \langle u_{DD}(r_{12}, \omega_1, \omega_2)\rangle_{\omega_1\omega_2} = \int [h(12) + 1]u_{DD}(12) \frac{d\omega_1}{4\pi} \frac{d\omega_2}{4\pi}. \tag{7}$$

and, using equation (3) for the truncated dipole–dipole interaction

$$u_{av}(r) = -\tfrac{2}{3}\mu^2 r^{-3} h^{112}(r) - \frac{2(\varepsilon' - 1)}{2\varepsilon' + 1} \frac{\mu^2}{3R_c^3} h^{110}(r). \tag{8}$$

For the short range structure of $h^{112}$ and $h^{110}$ and in the vicinity of the maxima of $h^{112}$, the reaction field term in equation (8) can be neglected, and then the following relation is obtained

$$u_{av}(r) \approx -\tfrac{2}{3}\mu^2 r^{-3} h^{112}(r). \tag{9}$$

From this expression one immediately sees that the maxima in $h^{112}(r)$ correspond to minima in the average dipole–dipole potential, and therefore one may
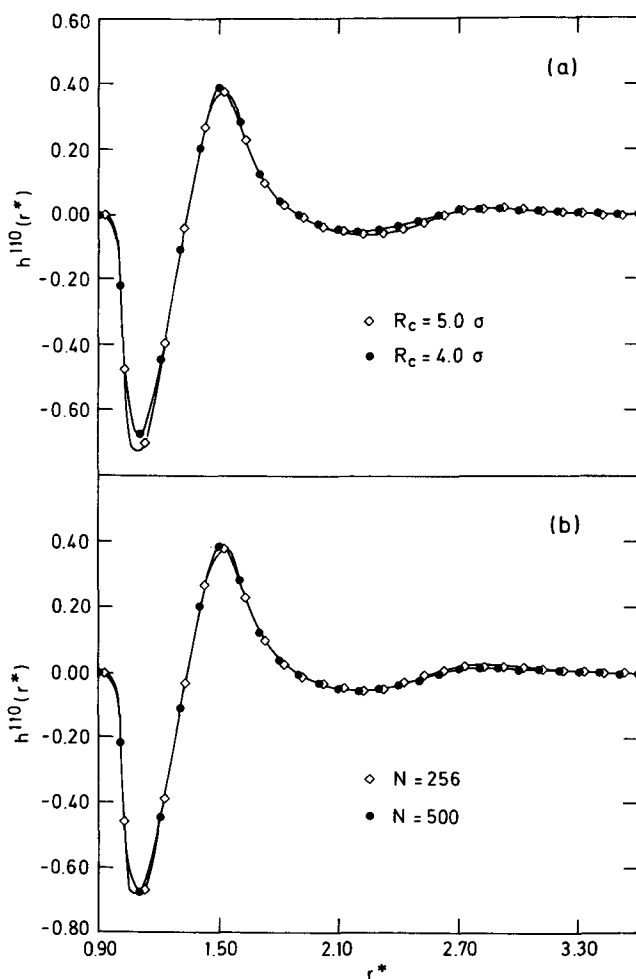
Figure 2.    The coefficient $h^{110}(r)$ (a) computed in a 500 particle sample with $R_c$ set to $4\sigma$ and $5\sigma$; (b) computed in 256 and 500 particle samples with $R_c = 4\sigma$.

predict the position of the different orientational layers; it is easy to realize that the first peak in $h^{112}(r)$ occurs at the same distance as the maximum in $h^{110}(r)$. This is equally true for the shoulder observable at $r \lesssim \sigma$ and the deep minimum in $h^{110}$. At this point it is worth note that at $\rho d^3 = 0.78$ ($\rho^* = 0.435$) the shoulder in $h^{112}$ is not found in the results of Morriss [9] for the point charge model. Probably the point dipole (ideal) increases the stability of the antiparallel layer (stability which is also observed if one compares in some detail our figure 1 with figure 1 of [9]). This effect may be explained in terms of the quadrupolar contribution to the multipole expansion of the point charge dipole, which is known to favour $T$-shaped configurations [15].

The results obtained by Steinhauser [3] for a model of acetonitrile (a three centre LJ point charge potential) exhibit very similar trends (in this case, the shoulder in $h^{110}$ is observable). This confirms that the orientational structure of fluids of this sort is due mainly to the shape forces than to the precise details of the intermolecular potential.

## 4. The influence of the sample size and cutoff radius

A great deal of work has been dedicated to determine the most adequate conditions (especially the sample size and—in RF computations—the cutoff radius $R_c$) in order to obtain consistent values of the dielectric properties in the simulation of dipolar fluids. Although it has been studied in some detail for samples of spherically shaped particles [2, 6, 7], to our knowledge the influence of these parameters on the results for molecular fluids has not been investigated so far. We will see that the molecular anisotropy alters well established results and conclusions for spherical models.

First, we must focus on the effects on the microscopic structure brought about by changes in the number of particles and in $R_c$. Since the $h^{110}(r)$ function is relevant to the dielectric properties we pay special attention to it. The influence of the cutoff radius $R_c$ can be observed in figure 2 (a) in which, at the same density ($\rho\sigma^3 = 0.435$) and in a 500 particle sample, the dipolar potential is truncated at $R_c = 4\sigma$ and $5\sigma$. In figure 2 (b) we show this coefficient at $\rho\sigma^3 = 0.435$ computed in samples of 256 and 500 particles (with $R_c = 4\sigma$). Both figures doubtless indicate that the orientational structure (at least at short and medium ranges) is not very sensitive to changes in any of these parameters. This result is striking since previous works [6, 13] had shown the existence of a pronounced dependence on $R_c$ for spherically shaped molecules treated in the RF approach.

As one goes from the microscopic to the macroscopic properties, the results become even more striking. In apparent contradiction with the conclusions of the preceding paragraph, for $g_k$ and $\varepsilon$ one can see (table 1) a remarkable $N$-dependence when samples of 256 or 500 particles are used at $\rho\sigma^3 = 0.435$. From figure 3 it is clear that these differences are at high densities, since at $\rho\sigma^3 = 0.3$ the results differ by little and at $\rho\sigma^3 = 0.2$ are indistinguishable. These differences may not be ascribed to the statistical uncertainty since the convergence of the results with the number of configurations is satisfactory. This plot also shows the insensitivity of these quantities to changes in $R_c$, which is in accordance with the lack of sensitivity of $h^{110}$. Furthermore, both results are in contrast with known features of the simulation of spherical dipolar particles. In particular, Pollock and Alder in their classical work on Stockmayer fluids [7] report a very slight dependence of $\varepsilon$ on the sample size (the differences are within a 10 per cent).

The relatively small dependence on $R_c$ can be explained in terms of the influence of the molecular shape, which induces a short range ordering and, thus, is very likely to minimize the small orientational effects due to increments in the range of the dipolar interactions. Actually, this effect has also been investigated by the authors within a theoretical approach by means of the RHNC equation [20]. Such results

Table 1. Dielectric properties for the dipolar hard dumbell fluid.

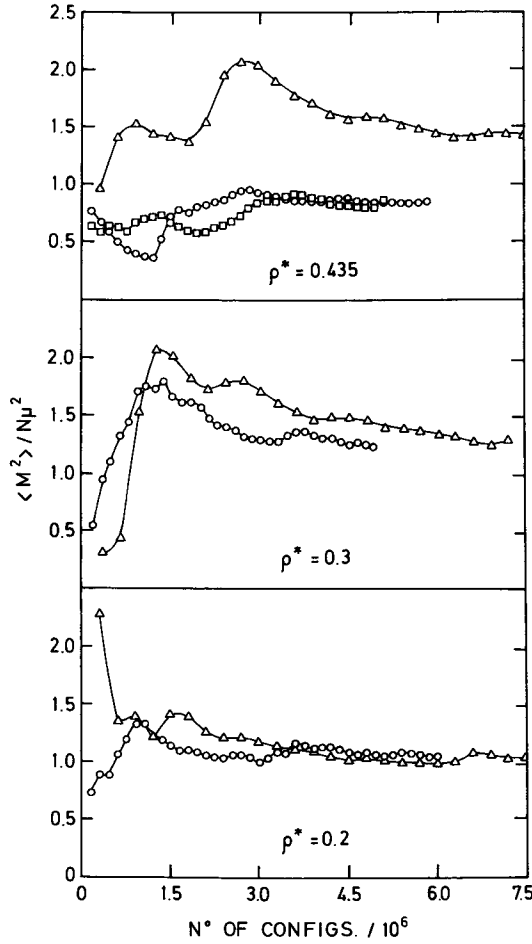| $\rho^*$ | $\langle M^2 \rangle / N\mu^2$ | | $\varepsilon$ | |
|---|---|---|---|---|
| | $N = 500$ | $N = 256$ | $N = 500$ | $N = 256$ |
| 0·2 | 1·05 ± 0·04 | 1·04 ± 0·03 | 3·2 ± 0·1 | 3·2 ± 0·1 |
| 0·3 | 1·31 ± 0·04 | 1·30 ± 0·03 | 5·1 ± 0·1 | 5·2 ± 0·1 |
| 0·43 | 0·85 ± 0·04 | 1·44 ± 0·04 | 4·9 ± 0·2 | 8·0 ± 0·2 |
| 0·5 | 0·63 ± 0·03 | — | 4·4 ± 0·1 | — |

Figure 3.   The convergence of $\langle M^2 \rangle / N\mu^2$ in Monte Carlo simulations with several sample sizes and cutoff radii: Triangles, $R_c = 4\sigma$ and 256 particles; circles, $R_c = 4\sigma$ and 500 particles; squares, $R_c = 5\sigma$ and 500 particles.

prove unambiguously that this feature cannot be considered an artifact of the simulation procedure. Hence, the values of $\varepsilon$ obtained for $R_c = 4\sigma$ and $5\sigma$ should be equivalent to the non-truncated potential results for $\varepsilon$.

There is another feature already seen in the theoretical study of these systems which could account for the $N$-dependence of $\varepsilon$. The contribution to $\varepsilon$ from the antiparallel and parallel layers almost exactly cancel and thus the value of this quantity is essentially determined by the long range structure. This is easily seen in figure 4, where the function

$$g_k(R) = 1 + \frac{4\pi}{3} \rho \int_0^R r^2 \, h^{110}(r) \, dr \tag{10}$$

is displayed. This function is expected to fulfil the limiting condition

$$\lim_{R \to \infty} g_k(R) = g_k = \langle M^2 \rangle / N\mu^2. \tag{11}$$

Thus, slight departures in the long range phase of the microscopic structure may lead to significant differences in $\varepsilon$, even if the whole structure seems to agree satisfac-
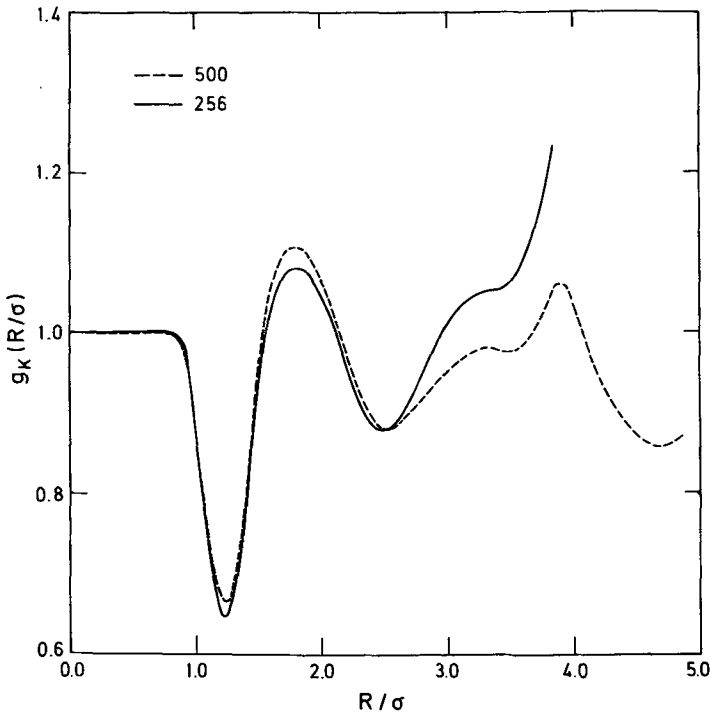
Figure 4. The $R$-dependent Kirkwood $g_k(R)$ factor (see equation (10)) computed in 256 and 500 particle samples at $\rho\sigma^3 = 0\cdot435$, and with $R_c = 4\sigma$.

torily as is now the case. In this way, the sample size dependence at rather high densities ($\rho d^3 \simeq 0\cdot8$) could be brought about by the presence of indirect angular correlations (via two or more particles) which, due to the pronounced short range orientational structure of the fluid, may introduce non-desirable self-interactions between any particle and its corresponding images in the neighbouring simulation cells. The important point is that the weight of the long range $h^{110}(r)$ is extremely enhanced by the molecular anisotropy which would explain the distinct $N$- and $R_c$-dependence of spherical and linear dipolar systems. Furthermore, these effects are obviously minimized when the size of the simulation cell is much greater than the cutoff radius. Hence, one cannot find such a dependence for $\rho\sigma^3 = 0\cdot3$ or $0\cdot2$. In our simulation at $\rho\sigma^3 = 0\cdot4352$ the ratio $R_c/L$ ($L$ side of the simulation cell) when using 500 particles is $0\cdot38$ for $R_c = 4\sigma$ close to the one at $\rho\sigma^3 = 0\cdot3$ ($0\cdot42$ for 256 sample particles and the same cutoff radius) and therefore one may expect that our results at the former density is sample size independent.

## 5. Macroscopic properties: dielectric constant and thermodynamics

The study of dipolar fluids is mainly aimed at the determination of dielectric properties, especially the dielectric constant $\varepsilon$. In non-polarizable fluids this quantity stems from the permanent dipolar moment $\mu$. In our sample, $\varepsilon$ is obtainable from equation (4), where the average

$$\langle M^2 \rangle / N\mu^2 = 1 + \frac{2}{N} \sum_{i>j}^{N} \langle \cos \theta_{ij} \rangle \tag{12}$$
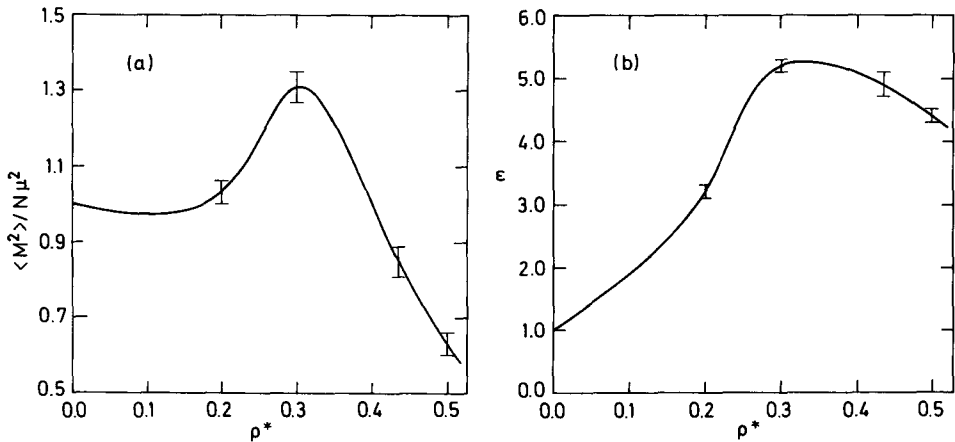
Figure 5.    Density dependence of $\langle M^2 \rangle / N\mu^2$ (a) and the dielectric constant, $\varepsilon$ (b).

can be evaluated throughout the simulation run. The numerical results for the Kirkwood, $g_k$, factor and $\varepsilon$ are shown in table 1 (as noted in the previous section several simulations using 256 and 500 sample particles were performed). In figure 5 the $\rho$-dependence of $g_k$ and $\varepsilon$ is depicted (the results correspond to 500 particle samples). Smooth lines connecting the simulated points have been drawn. The most remarkable feature in figure 5 is the decrease in $g_k$ once that $\rho\sigma^3$ reaches a certain value (corresponding to the liquid state, more or less). This effect is somewhat damped by equation (4) but it is nevertheless clearly noticeable in the $\rho$-dependence of $\varepsilon$.

We are not aware of any study of the density dependence of $\varepsilon$ (or $g_k$) in fluids of spherically shaped molecules. Previous works for such systems have focused mostly on the influence of the dipolar strength at a given density. Nevertheless, one may expect a similar dependence on both quantities (actually in the mean spherical approximation they are coupled into a single parameter $y$ [18]). This would imply a monotonic increase in $g_k$ and subsequently in $\varepsilon$ associated with an increasing $\rho\sigma^3$ (keeping $\mu^{*2}$ constant). This does not apply to the dipolar dumbell system, where we found a maximum both in $g_k(\rho)$ and in $\varepsilon(\rho)$ (see figure 5). Indeed, the low density behaviour does not differ significantly from the spherical case since one can expect that the effects of the molecular anisotropy should be minimized as the average interparticle distance is large. Once the system has reached a liquid density ($\rho\sigma^3 \gtrsim 0\cdot4$), the proximity of other non-spherical molecules in the sample introduces a steric hindrance to the rotation of the particles, in such a way that the reordering of the sample in the presence of an external electric field should be hindered. Therefore, the polarization of the sample decreases and so it does the dielectric constant. The presence of the steric hindrance is solely due to the molecular aniso-tropy, and it is responsible for the observed low values of the dielectric constant in model molecular fluids. The shape forces would cause the destruction of $\langle \mu_1 \cdot \mu_2 \rangle$ in real fluids as well [15], and thus there is no need to appeal to the effect of the quadrupole moment to explain the low $\varepsilon$ values observable in systems of anisotropic molecules.

The potential model used in this work can adequately represent the hard core interactions of $CH_3Cl$ [9]. The dielectric constants obtained for this molecular

model is, nonetheless, well below the experimental value (from table 1, $\varepsilon \simeq 5$ whereas the experimental value is $\varepsilon \simeq 12$ [9]). This difference can be explained as a consequence of deficiencies in the interaction potential, such as the use of a hard core potential and/or point dipoles. With regard to this latter instance, Morriss has obtained $\varepsilon \simeq 7$ for a point charge model [10], which represents a small improvement. It seems reasonable that the use of a soft core potential could improve the results in a noticeable way since the molecular reordering would be less hindered by such a potential. It should be recalled that slight changes in the predicted microscopic structure can be amplified for $\varepsilon$ due to the cancellation in the contributions of the antiparallel and parallel layers. In this way the effect of the quadrupolar interactions might be noticeable in the final value of the dielectric constant. Nevertheless, Steinhauser [3], using a three centre Lennard-Jones plus point charges model for acetonitrile found a value $g_k \to 0.9$, which means a result below the Onsager's $\varepsilon$ ($g_k = 1$). It is, however, known that the experimental value for this substance lies above the Onsager $\varepsilon$. The large discrepancy between the $\varepsilon$ for our model and the experimental one, could also stem from the neglect of the molecular polarizability. It is a well established result that the introduction of polarizability enlarges the value of $\varepsilon$, so that one may expect that this correction should force the simulation results closer to the experimental ones.
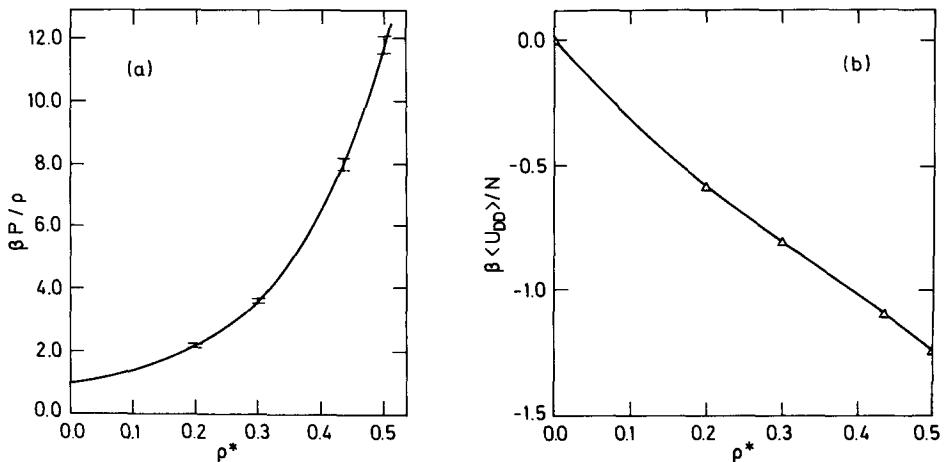


Figure 6. Density dependence of the compressibility factor (a) and configurational energy (b).

Table 2. Configurational energy and compressibility factor for the dipolar hard dumbell fluid. (HD) denotes uncharged hard dumbell values.

| | $\beta\langle U_{\mathrm{DD}}\rangle/N$ | | | |
|---|---|---|---|---|
| $\rho^*$ | $N = 500$ | $N = 256$ | $\beta P/\rho$ | $\beta P/\rho$ (HD) |
| 0·2 | −0·582 | −0·582 | 2·2 ± 0·07 | 2·47 |
| 0·3 | −0·807 | −0·813 | 3·6 ± 0·08 | 4·07 |
| 0·435 | −1·089 | −1·086 | 8·0 ± 0·19 | 8·56 |
| 0·5 | −1·233 | — | 11·8 ± 0·27 | 12·70 |

Considering the thermodynamic properties, in figure 6 and table 2 we present our results for the compressibility factor $\beta P/\rho$ and the configurational energy $\beta\langle U_{DD}\rangle/N$. The former quantity shows a behaviour quite similar to that exhibited by an uncharged hard dumbbell fluid; this could be expected since this quantity is mainly built into the shape forces. As in the spherical case [15], in table 2, where the uncharged dumbbell results are obtained by the Boublik–Nezbeda equation of state [19] and denoted by (HD), it can be seen that the net effect of the dipoles is a decrease in the value of $\beta P/\rho$. This means that the dipoles somehow stabilize the fluid. The configurational energy exhibits a rather linear dependence on density, which simply reflects the increase in the number of dipole–dipole interactions.

If one compares the simulated values of our point dipole model with that of the point charge dipolar fluid, one immediately sees that the differences are only quantitative, and relatively small. Actually, the $h^{1112m}(r)$ coefficients show very small discrepancies, and if one takes into account that the uncertainties in simulated $\varepsilon$ range from 15–21 per cent [3, 10] the difference between our $\varepsilon$ ($\simeq 5$) and the value obtained by Morriss [10] ($\varepsilon \simeq 7$) is not really meaningful. In the configurational energy (table 2 of this work and table 3 in [9]) the deviation rises to 8 per cent. Consequently, the two models are not so different as has been assumed so far [3, 10], even in rather dense and strongly coupled fluids.

### References

[1] DE LEEUW, S. W., PERRAM, J. W., and SMITH, E. R., 1980, *Proc. R. Soc.* A, **373**, 27.
[2] NEUMANN, M., and STEINHAUSER, O., 1980, *Molec. Phys.*, **39**, 437.
[3] STEINHAUSER, O., 1982, *Molec. Phys.*, **45**, 335.
[4] NEUMANN, M., STEINHAUSER, O., and PAWLEY, G., 1984, *Molec. Phys.*, **52**, 97.
[5] LEVESQUE, D., PATEY, G. N., and WEIS, J. J., 1977, *Molec. Phys.*, **34**, 1077.
[6] PATEY, G. N., LEVESQUE, D., and WEIS, J. J., 1982, *Molec. Phys.*, **45**, 733.
[7] POLLOCK, E. L., and ALDER, B. J., 1980, *Physica* A, **102**, 1.
[8] DE LEEUW, S. W., PERRAM, J. W., and SMITH, E. R., 1986, *A. Rev. phys. Chem.*, **37**, 245.
[9] MORRISS, G. P., and CUMMINGS, P. T., 1982, *Molec. Phys.*, **45**, 1099.
[10] MORRISS, G. P., 1982, *Molec. Phys.*, **47**, 833.
[11] EVANS, W. A. B., and POWLES, J. G., 1982, *Molec. Phys.*, **45**, 695.
[12] ISBISTER, D., and MORRISS, G. P., 1985, *Chem. Phys. Lett.*, **122**, 29.
[13] LADO, F., LOMBARDERO, M., ENCISO, E., LAGO, S., and ABASCAL, J. L. F., 1986, *J. chem. Phys.*, **85**, 2916.
[14] FRIES, P. H., and PATEY, G. N., 1985, *J. chem. Phys.*, **82**, 429.
[15] STELL, G., PATEY, G. N., and HOYE, J. S., 1981, *Adv. chem. Phys.*, **48**, 183.
[16] BARKER, J. A., and WATTS, R. O., 1969, *Chem. Phys. Lett.*, **3**, 144; 1973, *Molec. Phys.*, **26**, 789.
[17] NEUMANN, M., 1983, *Molec. Phys.*, **50**, 841.
[18] WERTHEIM, M. S., 1971, *J. chem. Phys.*, **55**, 4291.
[19] BOUBLIK, T., and NEZBEDA, I., 1977, *Chem. Phys. Lett.*, **46**, 315.
[20] LOMBA, E., LOMBARDERO, M., and ABASCAL, J. L. F., 1989, *J. chem. Phys.*, **91**, 2581.