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A comparison between computer simulation and theoretical results for fluids of dipolar soft spheres

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In this paper we report results determined by computer simulation and the reference hypernetted-chain (RHNC) and reference linearized HNC (RLHNC) integral equation theories for dipolar soft-sphere fluids. Comparison of values obtained indicates that the average energies, the pressures and the pair distribution functions given by both theories are reasonably accurate. The rather poor agreement found for the static dielectric constant is discussed. Computer simulation results for the closely related Stockmayer fluid are also included. The effect of the short-range potential upon the equilibrium and dynamical properties of these systems as well as its influence upon the accuracy of the RHNC and RLHNC approximations is examined.

1. Introduction

Computer simulation has become a very useful technique with which to test approximate theories. Dipolar fluids have been the subject of numerous theoretical studies because of the relative simplicitly of the models and because of a general interest in the microscopic behaviour of polar liquids. For these systems the comparison of simulation and theoretical results has focussed mainly upon two models, dipolar hard spheres [1–9] and Stockmayer particles [1, 9–11].

The computer simulation of polar fluids has several pitfalls which require careful attention [1, 12], particularly if the dielectric properties of the system are desired. The problems are a consequence of the long-range nature of the dipolar interactions and of the fact that only a relatively small number of particles (typically 10^2–10^3) can be considered in a simulation. Integral equation theories [1, 3–10] provide a straightforward, albeit approximate, means of obtaining infinite system results for dipolar fluids including the static dielectric properties. Closure approximations based upon the hypernetted-chain (HNC) relationship [13] have proven the most successful [1, 3, 10]. However, both the reference linearized HNC (RLHNC) [5] and the reference quadratic HNC (RQHNC) [14] theories overestimate the static dielectric constant for purely dipolar systems [1, 5, 8, 11], particularly for large dipole moments. It has been recently shown [3, 10] that the reference HNC (RHNC) theory significantly improves upon the previous approximations for dipolar hard-sphere and Stockmayer liquids. For both models the RHNC results for the static dielectric constant are generally in very good agreement with those of computer simulation.

In this article we report molecular dynamics (MD), RLHNC and RHNC results for fluids of soft-sphere particles with embedded point dipole moments. The structural, thermodynamic and dielectric properties will be examined and compared. The

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behaviour observed will also be contrasted with that obtained for the closely related Stockmayer systems.

The remainder of this paper is divided into three parts. In § 2 we describe the models considered, as well as briefly outlining the RHNC and RLHNC theories and the MD techniques used to study them. We discuss our results in § 3 and finally our conclusions are summarized in § 4.

2. Models and methods

For a fluid of purely dipolar particles the pair potential can be expressed as

$$u(12) = u_{SR}(r) + u_{dd}(12), \tag{1a}$$

where $u_{SR}(r)$ is some isotropic short-range interaction and the dipole–dipole interaction

$$u_{dd}(12) = \frac{-\mu^2}{r^3}\,\Phi^{112}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2, \hat{\mathbf{r}}), \tag{1b}$$

where μ is the dipole moment, r is the separation between particles 1 and 2, $\boldsymbol{\Omega}_1$ and $\boldsymbol{\Omega}_2$ represent the sets of Euler angles describing their orientation, and $\hat{\mathbf{r}}$ denotes the direction of $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. The rotational invariant $\Phi^{112}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2, \hat{\mathbf{r}})$ is defined by [3]

$$\Phi^{mnl}_{\mu\nu}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2, \hat{\mathbf{r}}) = f^{mnl} \sum_{\mu'\nu'\lambda'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} R^m_{\mu'\mu}(\boldsymbol{\Omega}_1) R^n_{\nu'\nu}(\boldsymbol{\Omega}_2) R^l_{\lambda' 0}(\hat{\mathbf{r}}), \tag{2}$$

where $\begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix}$ is a 3-j symbol, $R^m_{\mu'\mu}(\boldsymbol{\Omega})$ is a Wigner generalized spherical harmonic and f^{mnl} can be any non-zero constant. We remark that for simple dipolar fluids the lower indices of $\Phi^{mnl}_{\mu\nu}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2, \hat{\mathbf{r}})$ are always zero and hence for notational convenience have been suppressed in the present article. When represented in cartesian form

$$\Phi^{112}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2, \hat{\mathbf{r}}) = 3(\hat{\boldsymbol{\mu}}_1 \cdot \hat{\mathbf{r}})(\hat{\boldsymbol{\mu}}_2 \cdot \hat{\mathbf{r}}) - \hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2, \tag{3a}$$

for the choice

$$f^{mnl} = l!/\begin{pmatrix} m & n & l \\ 0 & 0 & 0 \end{pmatrix}, \tag{3b}$$

where $\hat{\boldsymbol{\mu}}_i$ is a unit vector denoting the direction of the dipole moment of particle i.

For dipolar hard spheres the spherically symmetric short-range interaction appearing in equation (1) is simply the hard-sphere potential, while for Stockmayer particles $u_{SR}(r)$ is the usual Lennard-Jones (LJ) potential given by [13]

$$u_{LJ}(r) = 4\varepsilon_{LJ}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{4a}$$

For the dipolar soft-sphere systems we have considered, we can write the short-range potential in the form [15]

$$u_{SS}(r) = 4\varepsilon_{SS}\left(\frac{\sigma}{r}\right)^{12}, \tag{4b}$$

which emphasizes its relationship to $u_{LJ}(r)$. We point out that like the hard-sphere interaction the soft-sphere potential is simpler than the LJ interaction in that it can be completely specified with only a single parameter [15].

(*a*) *Integral equation theory*

The methods of solution of the RHNC and RLHNC theories for simple dipolar liquids have been described in previous articles [3, 5]. Therefore, in this paper we will only briefly outline some of the basic definitions and essential relationships.

The RHNC and RLHNC theories consist of the Ornstein–Zernike (OZ) equation

$$h(12) = c(12) + \frac{\rho}{8\pi^2} \int h(13)c(32)d(3) \tag{5}$$

coupled with the appropriate closure approximation. In equation (5), $h(12)$ and $c(12)$ are the pair and direct correlation functions, respectively, of particles 1 and 2, $\rho = N/V$ is the number density, and $d(3)$ indicates integration over all the positional and orientational coordinates of particle 3. Following earlier work [16] we write the RHNC closure in the form

$$c(12) = h(12) - \ln g(12) - \beta u(12) + B_{\mathbf{R}}(r) \tag{6a}$$

in which $g(12) = h(12) + 1$ is the pair distribution function, $B_{\mathbf{R}}(r)$ refers to the bridge function of some spherically symmetric reference system, and $\beta = 1/kT$ where kT is the Boltzmann constant times the absolute temperature. By separating the pair potential into reference and perturbation parts, $u_{\mathbf{R}}(r)$ and $\Delta u(12)$, respectively, we can define the function

$$Y_{\mathbf{R}}(r) = B_{\mathbf{R}}(r) - \beta u_{\mathbf{R}}(r) = \ln g_{\mathbf{R}}(r) - \eta_{\mathbf{R}}(r), \tag{6b}$$

where $g_{\mathbf{R}}(r)$ and $\eta_{\mathbf{R}}(r) = h_{\mathbf{R}}(r) - c_{\mathbf{R}}(r)$ also refer to the spherically symmetric reference system. Equation (6*a*) can then be written as [3, 16]

$$c(12) = \int_r^\infty h(12) \frac{\partial W^{\mathbf{RHNC}}(12)}{\partial r} dr - \beta \Delta u(12) + Y_{\mathbf{R}}(r), \tag{6c}$$

where

$$W^{\mathbf{RHNC}}(12) = -\eta(12) + \beta \Delta u(12) - Y_{\mathbf{R}}(r). \tag{6d}$$

The reduction of the RHNC (and RLHNC) equations for fluids characterized by angle-dependent pair potentials is based upon the expansion of the pair interaction and correlation functions in a basis set of rotational invariants [3, 17] defined by equation (2). These expansions have the general form

$$a(12) = \sum_{\substack{mnl \\ \mu\nu}} a_{\mu\nu}^{mnl}(r) \Phi_{\mu\nu}^{mnl}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2, \hat{\mathbf{r}}). \tag{7}$$

In accord with previous studies [3–5, 8–10] all the correlation functions presented in this paper are for f^{mnl} as given by equation (3*b*). Again we point out that for simple dipolar systems only the terms for which $\mu\nu = 00$ are non-zero.

In § 3 we also report results obtained using the RLHNC approximation. For a pure liquid, if $\Delta u^{000}(r) = 0$ (as is the case here) then

$$c^{mnl}(r) = h_{\mathbf{R}}(r)[\eta^{mnl}(r) - \beta \Delta u^{mnl}(r)] - \beta \Delta u^{mnl}(r) \tag{8}$$

for $mnl \neq 000$ is sufficient to specify the RLHNC closure [3, 5]. Details of the reduction of the RLHNC and RHNC equations along with the methods used to find numerical solutions to these approximations can be found in previous articles [3, 19].

The application of the RHNC and RLHNC theories requires that the radial distribution function of the appropriate reference system be known. The thermodynamically consistent integral equation theory of Rogers and Young [18] appeared to be a convenient means of generating the required soft-sphere radial distribution function. Approximations based on the 'blip' function theory of Andersen *et al.* [15(b)] (such as the EXP approximation for LJ liquids) did not represent a viable option because they had previously been shown to be not particularly accurate for soft-spheres (because of the 'softness' of these particles). Some initial calculations were performed using $g_{SS}(r)$ obtained from the Rogers and Young theory. However, we have found that the RHNC and RLHNC results for the static dielectric constant (and to a much lesser extent for the energy and pressure) are very sensitive to $g_{SS}(r)$, particularly for large dipole moments where variations as large as 35 per cent were observed. We remark that a similar sensitivity has been reported for Stockmayer fluids [10]. Consequently, 'exact' computer simulation values for $g_{SS}(r)$ were used to determine all the theoretical results presented in § 3. To generate $g_{SS}(r)$, a simulation of a soft-sphere fluid at the required temperature and density was carried out for 256 particles. The calculation was performed using techniques consistent with those outlined below with a reduced timestep of 0·004. A run length of 700 000 timesteps was sufficient to obtain $g_{SS}(r)$ to an accuracy of better than 0·1 per cent (except at very small separations, i.e. $r/\sigma \leqslant 0{\cdot}92$) on a numerical grid of width $\Delta r/\sigma = 0{\cdot}01$.

In § 3 we report RHNC and RLHNC estimates for the configurational energy, pressure and static dielectric constant. The average configurational energies per particle are given by

$$\frac{\langle U \rangle}{N} = \frac{\langle U_{SR} \rangle}{N} + \frac{\langle U_{DD} \rangle}{N}, \tag{9a}$$

where the short-range and dipole–dipole contributions, $\langle U_{SR} \rangle / N$ and $\langle U_{DD} \rangle / N$, respectively, were determined from the expressions

$$\frac{\langle U_{SR} \rangle}{N} = 2\pi\rho \int_0^\infty r^2 g^{000}(r) u_{SR}(r)\, dr \tag{9b}$$

and

$$\frac{\langle U_{DD} \rangle}{N} = \frac{-4\pi}{3} \rho\mu^2 \int_0^\infty h^{112}(r)/r\, dr. \tag{9c}$$

The average pressures were obtained from the compressibility factors which were calculated using the relationship

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi}{3} \beta\rho \int_0^\infty r^3 \frac{\partial u_{SR}(r)}{\partial r} g^{000}(r)\, dr + \frac{\beta \langle U_{DD} \rangle}{N}. \tag{10}$$

The usual Kirkwood formula [1]

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = yg, \tag{11a}$$

where

$$g = 1 + \frac{4\pi}{3} \rho \int_0^\infty r^2 h^{110}(r)\, dr \tag{11b}$$

and

$$y = 4\pi\rho\mu^2/9kT, \tag{11 c}$$

was used to determine the RHNC and RLHNC results for the static dielectric constant, ε.

(*b*) *Computer simulation*

A detailed description of the computer simulation techniques we have employed in the present study of polar fluids will be given elsewhere [20]. Hence, we again only briefly outline the essential points.

The MD calculations were performed with 256 particles in periodic boundary conditions (PBC). The long-range dipole–dipole interactions were evaluated using the Ewald summation technique. In this case $u_{dd}(12)$ becomes [21]

$$u_{dd}^{PBC;\,\varepsilon'}(12) = -(\boldsymbol{\mu}_1 \cdot \nabla)(\boldsymbol{\mu}_2 \cdot \nabla)\psi(\mathbf{r}) + \frac{4\pi}{(2\varepsilon' + 1)L^3}\,\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2, \tag{12 a}$$

in which

$$\psi(\mathbf{r}) = \frac{1}{L}\sum_{\mathbf{n}} \frac{\operatorname{erfc}(\alpha|\mathbf{r}/L + \mathbf{n}|)}{|\mathbf{r}/L + \mathbf{n}|} + \frac{1}{\pi L}\sum_{\mathbf{n}\neq 0}\frac{1}{n^2}\exp\left(\frac{-\pi^2 n^2}{\alpha^2} + \frac{2\pi i}{L}\,\mathbf{n}\cdot\mathbf{r}\right) \tag{12 b}$$

is the usual function associated with Ewald conducting boundary conditions [21, 22] and ε' is the dielectric constant of the continuum surrounding a macroscopic spherical sample that consists of a very large number of periodic replicas of the simulation cell. In equations (12) L is the length of the cubic simulation cell, the sum on $\mathbf{n} = (k, l, m)$ is a lattice sum, erfc is the complementary error function, and α is an adjustable convergence parameter. In our simulations the real space sum (first term) in equation (12 *b*) was carried over all nearest images, while the reciprocal space sum (second term) included all vectors for which $n^2 \leqslant 38$. A choice of $\alpha = 5{\cdot}75$ ensured that the total dipole–dipole energy for several sample configurations was accurate to better than one part in 10^5. Moreover, the requirement [23]

$$q = \frac{\alpha^3}{\pi^{3/2}}\int_V \exp\left(\frac{-\alpha^2 r^2}{L^2}\right) d\mathbf{r} = 1, \tag{13}$$

where in the present case V is just the volume of the simulation cell, is satisfied to better than 0·02 per cent.

The dielectric constants we report in § 3 were obtained using the formula [21, 24]

$$\frac{(\varepsilon - 1)(2\varepsilon' + 1)}{2\varepsilon' + \varepsilon} = \frac{4\pi}{3}\frac{\langle M^2\rangle}{VkT}, \tag{14}$$

in which $\langle M^2\rangle$ is the mean square moment of the simulation cell. In using equation (14) we have assumed that $\langle M\rangle^2 = 0$. We remark that for all our MD results, $\langle M\rangle^2$ is very small compared to $\langle M^2\rangle$ (i.e. $\sim 0{\cdot}7$ per cent for $\varepsilon' = \infty$, $\sim 0{\cdot}1$ per cent for $\varepsilon' \approx \varepsilon$).

The MD simulations were carried out at constant *temperature* by employing gaussian isokinetic equations of motion [25–27] to fix the *total* kinetic energy, as described in [20]. The equations of motion were integrated using a 4th order Gear

algorithm [25] for both the translational and rotational degrees of freedom, where the orientational coordinates have been expressed in terms of quaternion parameters [28].

3. Results and discussion

In our calculations and in the following discussion all molecular and state parameters are expressed in reduced units. The polar fluids we have considered can be characterized by

$$\rho^* = \rho\sigma^3, \tag{15a}$$

$$T^* = kT/\varepsilon_{SR} \tag{15b}$$

and

$$\mu^* = (\mu^2/\varepsilon_{SR}\,\sigma^3)^{1/2}, \tag{15c}$$

where ρ^*, T^* and μ^* are the reduced density, temperature and dipole moment, respectively, and ε_{SR} can be either ε_{LJ} or ε_{SS}. MD simulations were performed for Stockmayer and dipolar soft-sphere liquids at $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* = 1{\cdot}65$, both at $\varepsilon' = \infty$ and at $\varepsilon' \approx \varepsilon$. We remark that the Stockmayer system has been the subject of earlier simulation studies [11, 29, 30]. RHNC calculations for dipolar soft spheres were carried out for a range of dipole moments (see table 1), while the RLHNC approximation was solved only for the case $\mu^* = 1{\cdot}65$. RHNC and RLHNC results for Stockmayer particles can be found in [10].

All RHNC and RLHNC computations were performed on a numerical grid of 1024 points of width $\Delta r/\sigma = 0{\cdot}02$. As was done in previous theoretical studies of soft multipolar systems [9, 10], it was assumed that for $r/\sigma \leqslant d$, where d is some effective hard-sphere diameter, $g(12) = 0$ and equations (6) and (8) were replaced with

$$c(12) = 1 + \eta(12). \tag{16}$$

For the dipolar soft-sphere fluids considered in the present study, a value of $d = 0{\cdot}88$ was found to have a negligible influence upon the thermodynamic and dielectric properties. In order to carry out numerical calculations, the rotational invariant expansion (as given by equation (7)) must be truncated. Following earlier work [3, 10, 16] we have used the restriction $m, n \leqslant n_{max}$ to generate a finite RHNC basis set. The basis set dependence for dipolar soft spheres was found to be very similar to that observed for dipolar hard-sphere [3] and Stockmayer [10] fluids. The results given in this article were obtained using basis sets sufficiently large to ensure reasonable convergence of the properties of interest (i.e., $n_{max} = 3$ for all but

Table 1. RHNC results for dipolar soft-sphere fluids at $\rho^* = 0{\cdot}8$ and $T^* = 1{\cdot}35$.

μ^*	$\langle U_{DD}\rangle/N\varepsilon_{SS}$	$\langle U\rangle/N\varepsilon_{SS}$	$P\sigma^3/\varepsilon_{SS}$	ε
1·5	−2·61	2·48	15·26	24·4
1·65	−3·39	1·73	14·77	39·6
1·75	−3·96	1·10	14·11	56·1
1·9	−4·97	0·20	13·66	116
1·917	−5·09	0·10	13·61	130

the smallest dipole moment examined). Numerical solutions were found by iteration as discussed in [3] and [19].

The MD simulations each consisted of an equilibration of at least 20 000 timesteps followed by a run of 100 000 timesteps. A reduced timestep $\Delta t/\sqrt{(m\sigma^2/\varepsilon_{SR})} = 0{\cdot}0025$ was used to solve the equations of motion and the moment of inertia I was taken as $0{\cdot}025\,m\sigma^2$, where m refers to the particle mass. For both the Stockmayer and dipolar soft-sphere models, $u_{SR}(r)$ was truncated at $2{\cdot}56\,\sigma$ and the appropriate tail corrections were added to the energies and pressure. For the simulations in which $\varepsilon' \approx \varepsilon$, values of 31·5 and 32·2 were employed for the Stockmayer and dipolar soft-sphere systems, respectively, after having been 'determined' by the $\varepsilon' = \infty$ runs. Further computational details will be given in [20].

(*a*) *Thermodynamic and dielectric properties*

RHNC results for the average dipole–dipole and average total configurational energies, the pressure, and the static dielectric constant are given in table 1 for the dipole moments which we have examined. In table 2 values for $\langle U_{DD}\rangle/N\varepsilon_{SR}$, $\langle U\rangle/N\varepsilon_{SR}$, $P\sigma^3/\varepsilon_{SR}$, and ε obtained from the RHNC and RLHNC theories and from our two simulations for a dipolar soft-sphere fluid at $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* = 1{\cdot}65$ are compared. MD results for Stockmayer particles at an 'equivalent' state point are also included in table 2. We remark that the error bars for ε given in table 2 for the MD calculations were determined by examining block averages taken over 25 000 timesteps. We also note that any difference in $\varepsilon' = \infty$ and $\varepsilon' \approx \varepsilon$ simulation results for the thermodynamic properties is within the numerical accuracy. If we assume [31] that the static dielectric constant obtained is also independent of ε', we have $\varepsilon = 32 \pm 1$ and 31 ± 1 for the dipolar soft-sphere and Stockmayer systems, respectively.

It can be seen from table 2 that the RLHNC and RHNC energies are in fair agreement with the MD simulations. The RLHNC theory gives a better result than the RHNC for $\langle U_{DD}\rangle/N\varepsilon_{SS}$, while the opposite is true for $\langle U\rangle/N\varepsilon_{SS}$. The RHNC and RLHNC values for the pressure also compare well with the MD calculations, with the RHNC estimate being more accurate. However, we find that for the dielectric constant the agreement between the theories and computer simulation is rather poor, the RLHNC seriously overestimating ε.

The computer simulation results for the thermodynamic properties of the Stockmayer fluid given in table 2 agree very well with previous studies [11, 29, 30]. The value for the dielectric constant, $\varepsilon = 31 \pm 1$, is in accord with those of Pollock and

Table 2. Comparison of RHNC, RLHNC, and MD results for a dipolar soft-sphere fluid at $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* = 1{\cdot}65$. Also included are the values obtained from MD simulations of the equivalent Stockmayer system.

	Dipolar soft-sphere				Stockmayer	
Property	RLHNC	RHNC	MD($\varepsilon' = \infty$)	MD($\varepsilon' \approx \varepsilon$)	MD($\varepsilon' = \infty$)	MD($\varepsilon' \approx \varepsilon$)
$\langle U_{DD}\rangle/N\varepsilon_{SR}$	−3·54	−3·39	−3·578	−3·571	−3·884	−3·885
$\langle U\rangle/N\varepsilon_{SR}$	1·36	1·73	1·570	1·577	−8·862	−8·860
$P\sigma^3/\varepsilon_{SR}$	13·92	14·77	14·691	14·693	0·817	0·841
ε	90·3	39·6	32·2 (±1·2)	31·6 (±1·5)	30·6 (±0·9)	32·0 (±1·3)

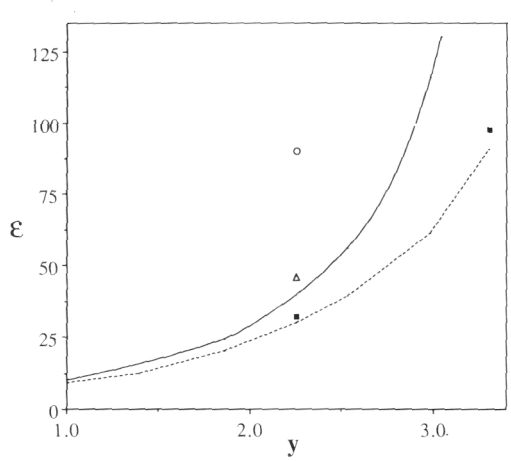

Figure 1. A comparison of different estimates for the static dielectric constant for Stockmayer and dipolar soft-sphere fluids at $\rho^* = 0{\cdot}8$ and $T^* = 1{\cdot}35$. The solid and dashed lines are RHNC results for the dipolar soft-sphere and Stockmayer [9, 10] systems, respectively, while the RLHNC estimates are indicated by the open circle and triangle. The solid squares are values obtained from MD calculations, the point at $y = 3{\cdot}308$ being our best estimate for the infinite system result [20].

Alder [11] and Levesque and Weis [30], but is larger than that reported by de Leeuw, Perram and Smith [29]. Moreover, it is obvious from table 2 that the Stockmayer and dipolar soft-sphere fluids have very similar static dielectric constants, the latter possibly having a slightly larger value. The absence of the attractive $1/r^6$ tail in $u_{SR}(r)$ for the dipolar soft-sphere model has a rather large effect upon the total energy and the pressure, as we would expect.

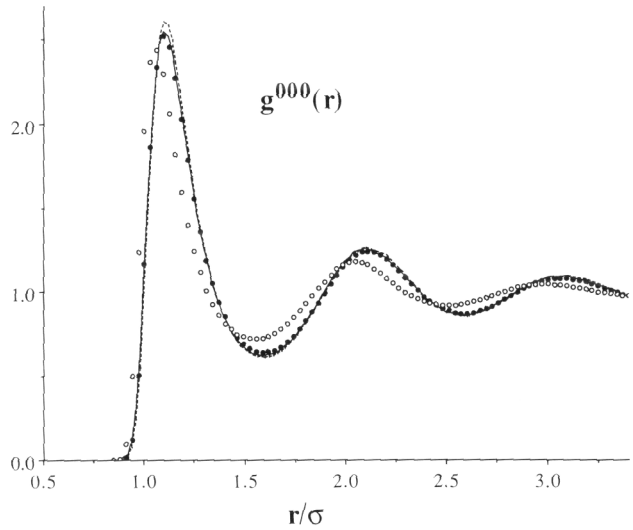

Figure 2. The radial distribution function, $g^{000}(r)$, at $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* = 1{\cdot}65$. The solid and dashed curves represent, respectively, RHNC and RLHNC results for dipolar soft spheres. The dots and open circles are values obtained from MD($\varepsilon' \approx \varepsilon$) simulations for dipolar soft-sphere and Stockmayer fluids, respectively.

It is clear from table 1 that for $\mu^* \geqslant 1{\cdot}9$ the RHNC estimate for ε grows very rapidly with increasing dipole moment. (This may well explain why we were unable to obtain a RHNC solution for $\mu^* = 2{\cdot}0$.) This fact can also be readily observed from figure 1 in which we have plotted ε as a function of y. Shown in figure 1 are RHNC and RLHNC results for the present dipolar soft-sphere fluids along with those obtained with Stockmayer particles [9, 10]. We have also included values as determined from MD simulations of dipolar soft spheres (the $\mu^* = 2{\cdot}0$ result will be discussed in detail in a future article [20]). We recall that in [10] the RHNC estimates for ε were found to be in very good agreement with computer simulation for Stockmayer fluids in which $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* \leqslant 1{\cdot}9$. However, at slightly higher density and lower temperature the agreement became rather poor. From figure 1 it is obvious that the RHNC and RLHNC theories are much less accurate for dipolar soft spheres than for Stockmayer particles, at least for the density and temerature we have examined.

(*b*) *The pair distribution function*

The three most interesting terms in the rotational invariant expansion of $g(12)$ (see equation (7)) are for $mnl = 000$, 110 and 112. In figures 2–4 we have plotted the radial distribution, $g^{000}(r)$, and the projections $h^{110}(r)$ and $h^{112}(r)$. MD($\varepsilon' \approx \varepsilon$), RHNC and RLHNC results for dipolar soft spheres at $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* = 1{\cdot}65$ are shown in each figure. Also included for comparison are the projections from our MD($\varepsilon' \approx \varepsilon$) simulation of the equivalent Stockmayer fluid. We remark that pair distribution functions from our $\varepsilon' \approx \varepsilon$ calculations should correspond most closely to those of the infinite systems, and hence are the most appropriate for comparison with the RHNC and RLHNC theories.

It can be seen in figure 2 that the RHNC and computer simulation results for $g^{000}(r)$ are in very good agreement. The radial distribution function given by the RLHNC theory, which is simply that of the soft-sphere reference system, differs only

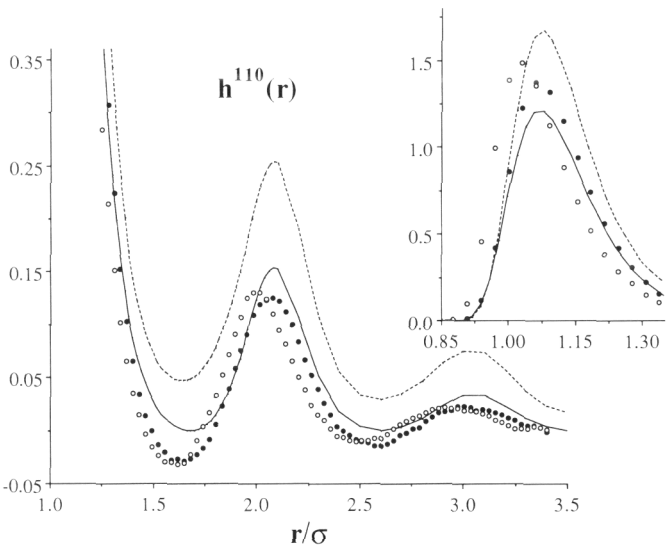

Figure 3. The projection $h^{110}(r)$ at $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* = 1{\cdot}65$. The curves and symbols are defined as in figure 2.

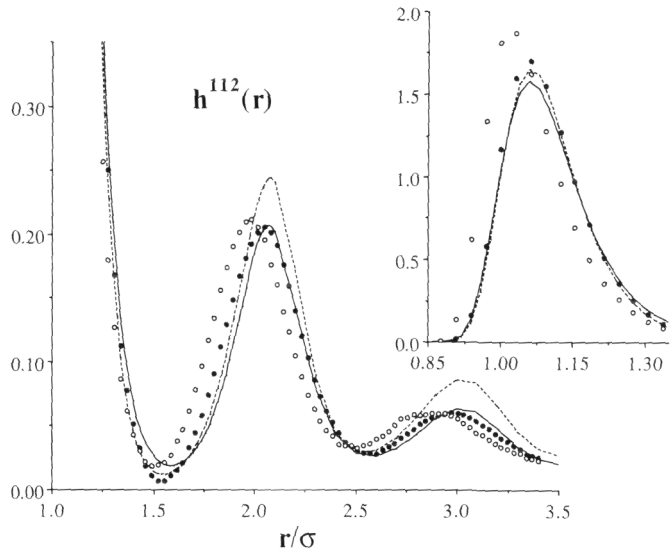

Figure 4. The projection $h^{112}(r)$ at $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* = 1{\cdot}65$. The curves and symbols are defined as in figure 2.

slightly from $g^{000}(r)$ determined from our MD calculations. It is also clear from figure 2 that the radial distribution function for the dipolar soft-sphere and Stockmayer fluids differ in at least two ways. Not only is $g^{000}(r)$ more structured for dipolar soft spheres, but the whole function appears to be shifted by a constant *scale factor* to large seprarations. These two observations would indicate that the dipolar soft-sphere model has a larger 'effective' diameter and is at a higher 'effective' density than the Stockmayer particles.

The projection $h^{110}(r)$ is shown in figure 3. We recall that $h^{110}(r)$ can be used to determine the dielectric constant (cf. equation (11)). In general the RHNC result lies below the RLHNC curve and is in much better agreement with the MD calculation, this behaviour being consistent with that observed for ε. Very similar behaviour has been found for Stockmayer systems [10]. However, we point out that in figure 3 the RHNC estimate for $h^{110}(r)$ appears shifted up from the simulation curve for $r/\sigma > 2{\cdot}0$ although this is not the case for the Stockmayer fluid (cf. figure 4 of [10]). It can also be seen from figure 3 the MD results for $h^{110}(r)$ are quite similar for dipolar soft spheres and Stockmayer particles when the larger 'effective' diameter of the former is taken into account.

In figure 4 we have plotted the projection $h^{112}(r)$ which gives the dipole–dipole energy (cf. equation (9*c*)). With the exception of the first peak we again find that the RHNC estimate is superior to that of the RLHNC, which is also consistent with the earlier study [10] of Stockmayer fluids. Comparing $h^{112}(r)$ for the dipolar soft-sphere and Stockmayer models we find very similar behaviour if we again ignore the shift in the results.

(*c*) *Time-correlation functions*

In figure 5 we present the normalized time-correlation function for the total dipole moment of the sample,

$$\Phi(t) = \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle / \langle M^2 \rangle, \tag{17a}$$

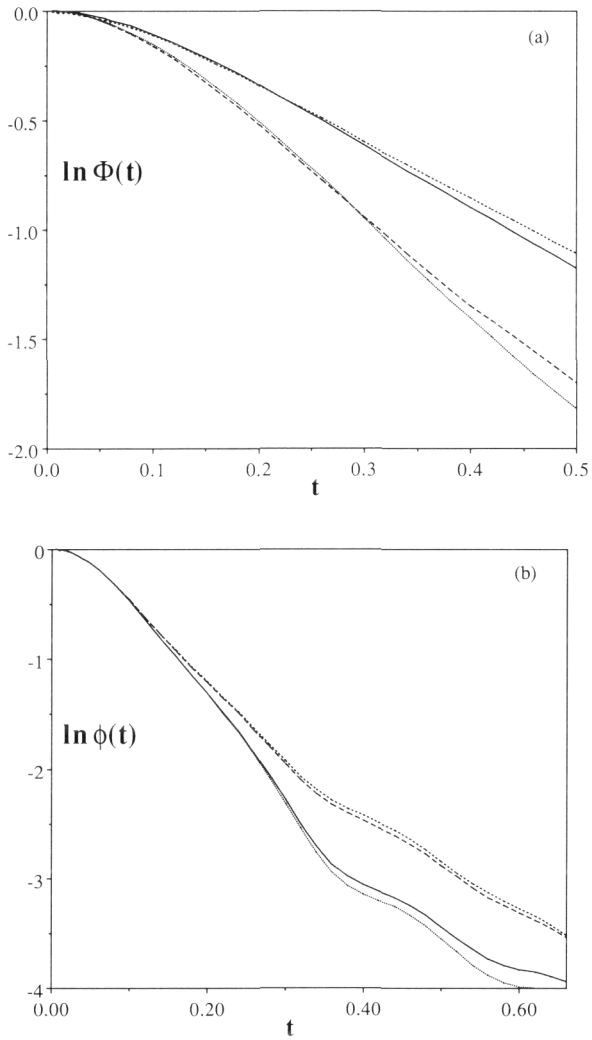

Figure 5. (*a*) The total-dipole time-correlation function for dipolar soft-sphere and Stockmayer fluids at $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* = 1{\cdot}65$. The solid and dotted curves are dipolar soft-sphere results for $\varepsilon' = \infty$ and 32·2, respectively, while the short and long dashed lines represent $\Phi(t)$ for the Stockmayer system with $\varepsilon' = \infty$ and 30·5, respectively. (*b*) The single-dipole time-correlation function. The curves are defined as in (*a*).

along with the analogous single-dipole autocorrelation function

$$\phi(t) = \langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0) \rangle / \mu^2. \tag{17 b}$$

We remark that these dynamical properties cannot be obtained from the RHNC and RLHNC theories, but can be directly determined in an MD simulation. We also point out that it is the logarithms of $\Phi(t)$ and $\phi(t)$ which have been plotted in figure 5 and the times given are expressed in reduced units.

It can be seen from figure 5(*a*) that after an initial non-exponential region, $\Phi(t)$ becomes purely Debye-like for both models, decaying as a single exponential to within numerical accuracy. This result agrees with those of previous workers [32,

33]. In accord with Neumann *et al.* [33, 34] the relaxation times for $\Phi(t)$ are larger for $\varepsilon' = \infty$ than for $\varepsilon' \approx \varepsilon$. We also find that for both $\varepsilon' = \infty$ and $\varepsilon' \approx \varepsilon$ the relaxation time for the dipolar soft-sphere system is slightly shorter than for the Stockmayer fluid.

From figure 5(*b*) we observe that the single-dipole time-correlation function decays much more rapidly than $\Phi(t)$, indicating the importance of collective effects in these fluids. Like $\Phi(t)$, $\phi(t)$ becomes exponential after a short inertial region. However, as can be clearly seen in figure 5(*b*), we find that at longer times (i.e. $t \geqslant 0{\cdot}3$) non-exponential dependence is again evident. This behaviour, which can be seen in previous work (cf. figure 1 of [32]), is more pronounced for dipolar soft spheres. Finally, although we might expect $\phi(t)$ to be independent of ε', some dependence is apparent at longer times (again for $t \geqslant 0.3$). The influence of ε' upon both $\Phi(t)$ and $\phi(t)$ will be explored in greater detail in a subsequent article [20].

4. Conclusions

In this paper we have examined and compared computer simulation and theoretical results for dipolar soft spheres. The average energies, pressures, static dielectric constants, and pair distribution functions were all considered. MD calculations were also performed for the closely related Stockmayer fluid and comparisons were made between the two models.

For $g(12)$ the theoretical estimates and MD were found to be in good agreement for the particular dipolar soft-sphere fluid we have investigated. In general, the RHNC gave better results for the radial distribution function and the projections $h^{110}(r)$ and $h^{112}(r)$ than the RLHNC approximation. When compared with $g^{000}(r)$, $h^{110}(r)$ and $h^{112}(r)$ obtained for Stockmayer particles, the curves for dipolar soft spheres demonstrate behaviour indicating that the latter have a larger 'effective' diameter and are at a higher 'effective' density.

For the dipolar soft-sphere system we have considered, the RHNC and RLHNC theories give quite reasonable estimates for the thermodynamic properties. However, both approximations were in rather poor agreement with MD results for the static dielectric constant; the RLHNC was found to overestimate ε by a factor of about three. This was somewhat unexpected since the RHNC had been previously [10] shown to yield a dielectric constant in good agreement with computer simulation for a Stockmayer fluid at the equivalent state point. Our MD calculations at $\rho^* = 0{\cdot}8$, $T^* = 1{\cdot}35$ and $\mu^* = 1{\cdot}65$ gave values of $\varepsilon = 32 \pm 1$ and 31 ± 1 for the dipolar soft-sphere and Stockmayer systems, respectively. Clearly, the attractive $1/r^6$ tail in $u_{SR}(r)$ has little effect upon the static dielectric properties of these models, but does appear to greatly influence the ability of the RHNC and RLHNC approximations to predict ε. We can suggest two possible explanations for why the RHNC and RLHNC theories give rather poor estimates for ε for the present dipolar soft-sphere fluid. One possibility is the higher 'effective' density of this system. This suggestion would be consistent with the results of Lee *et al.* [10] who found that for Stockmayer particles the RHNC appeared to be less accurate for ε at a higher density and lower temperature. A second possibility is the 'softness' of the soft-sphere potential. This feature of $u_{SS}(r)$ has also made the development of an accurate theory for simple soft-sphere fluids more difficult than for WCA or LJ particles [15, 18]. Clearly, further studies are required in which different densities and temperatures and different short-range potentials are investigated.

We have also compared some of the dynamical properties of the dipolar soft-sphere and Stockmayer systems. For both fluids the total-dipole time-correlation function demonstrated Debye-like behaviour at long times, while the single-dipole function exhibits a simple exponential decay only for moderate times. Finally, we have observed that even $\Phi(t)$ and $\phi(t)$ have a clear dependence upon $u_{SR}(r)$.

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[31] We know that in the thermodynamic limit ε must be independent of ε' and N. The MD simulations of Pollock and Alder [11] indicate that at least for Stockmayer fluids for which $\mu^* \leqslant 1{\cdot}75$, 2·56 particles in PBC are sufficient to give infinite system results for ε. Thus it would seem reasonable to assume that the present values for ε are also

independent of ε'. However, very recent MD calculations [20] for the same dipolar soft-sphere fluid except with $\mu^* = 2{\cdot}0$ strongly suggest that this assumption does not hold for larger dipole moments.

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