

Monte Carlo simulations of dipolar and quadrupolar linear Kihara fluids. A test of thermodynamic perturbation theory

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Several simulations of dipolar and quadrupolar linear Kihara fluids using the Monte Carlo method in the canonical ensemble have been performed. Pressure and internal energy have been directly determined from simulations and Helmholtz free energy using thermodynamic integration. Simulations were carried out for fluids of fixed elongation at two different densities and several values of temperature and dipolar or quadrupolar moment for each density. Results are compared with the perturbation theory developed by Boublík for this same type of fluid and good agreement between simulated and theoretical values was obtained especially for quadrupole fluids. Simulations are also used to obtain the liquid structure giving the first few coefficients of the expansion of pair correlation functions in terms of spherical harmonics. Estimations of the triple point temperature to critical temperature ratio are given for some dipole and quadrupole linear fluids. The stability range of the liquid phase of these substances is shortly discussed and an analysis about the opposite roles of the dipole moment and the molecular elongation on this stability is also given.

1. Introduction

The study of the liquid state and, in particular, molecular liquids has relevant scientific and technological interest. The key to the large successes of study in this field must be mainly attributed to the rapid powerful computer developments to solve the complex mathematical tasks that this field of study requires. In particular, the integral equations have supplied results of great accuracy in the case of monatomic liquids [1]. The technique on the other hand is very complicated in the case of polyatomic liquids [2–4] and the most used approximation in this case has been the thermodynamic perturbation theory (PT) in its different variants [5–7]. The essential idea in these types of theories is that the structure of the system is given fundamentally by the intermolecular repulsive forces. In this case, an expansion about a reference system that only contains these forces permits one to find, with relative precision and ease, the properties of the system of interest [6]. However, perturbation theories fail when applied to systems

where the role of attractive forces is important as happens in systems with considerable dipolar or quadrupolar interactions. There is, however, also in this field more or less successful attempts [8] and one of these relatively recent attempts due to Boublík [9, 10] seems particularly promising when applied to linear fluids interacting according to a Kihara intermolecular potential [11]. Unfortunately, the theory of Boublík has not been proven directly up to now but through similar models [12] and intermediate approximations [13] what throws certain doubts on its range of validity. On the other hand, another well known liquid study method is a computer simulation [14] that permits one to compare directly models with experimental results. In particular, ourselves have accomplished extensive simulations using the Kihara linear model with and without multipoles [15–17] and these have been shown to be very efficient when obtaining experimental properties from real liquids, especially the liquid–vapour equilibrium [18]. Simulation is more expensive than theory in economic terms [19] and furthermore permits a smaller data reduction but its other capacities permits one to check theories in an unambiguous way. Taking this last aspect

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into account, the principal purpose of this work is to prove whether the theory proposed by Boublík [9] is actually valid and in what experimental range it may be confidently applied. For this goal, we have simulated linear models in the canonical ensemble in the same thermodynamic states and elongation used by Boublík and we have accomplished a systematic comparison between theory and simulation. Furthermore, we have obtained the contribution to internal energy and to Helmholtz free energy coming from the multipolar interaction and we have proven that these magnitudes follow similar empirical laws to those found by Vega and Gubbins [20] for a similar model of different elongation. We have found that agreement is good overall, specially for the internal energy at high densities and all the multipole moments. Results for the compressibility factor also agree well but simulations for high quadrupole moments show a discontinuity at high densities and low temperatures that is not predicted by PT. We have also tried to search for the reasons of success of PT, obtaining in our simulations the first few spherical harmonics of the expansion of the pair correlation function (PCF) and some suggestions are given. Keeping this in mind, we present the work as follows: section 2 is devoted to the model description, the conditions of the simulation and the related principal equations we make use of. Section 3 first presents the results of the simulation for quadrupolar fluids and then for dipolar fluids comparing them with the results obtained with the theory from Boublík. A discussion follows where the validity of Boublík's theory is analysed and where values of the thermodynamic properties for some other models are predicted on the basis of a recent definition of the reduced multipole densities [16, 17] for those where we have found that a law of corresponding states is well fulfilled. A short discussion about the stability range of dipole and quadrupole liquids in terms of the ratio of temperatures at triple and critical points as a function of the multipole moments is also given here. Finally, it is shown that dipole moment and molecular elongation have opposite influences on the dielectric constant and Kirkwood factors. A few additional remarks in the section 4 close the paper.

2. Potential model and simulation conditions

We consider here linear rods of length L mimicking linear or pseudolinear molecules [18]. Rods interact following a Kihara potential which is written as:

$$u_{12}^K = 4\varepsilon[(\sigma/\rho)^{12} - (\sigma/\rho)^6], \quad (1)$$

where ε and σ are parameters with energy and length dimensions, respectively, $\rho(\mathbf{r}, \omega_1, \omega_2)$ is the shortest distance between the molecular cores modelling the mol-

ecular shape. $\rho(\mathbf{r}, \omega_1, \omega_2)$ depends in a non-trivial way on positions and mutual orientations of molecules but, for the sake of simplicity, we denote it simply as ρ . The molecular core is a rod in all cases considered here. The reduced length of this rod is $L^* = L/\sigma$ for the models. Moreover, the pair interaction may contain electrostatic terms corresponding to point dipoles or quadrupoles, namely in a general way:

$$u = u_{12}^K + u^{\mu\mu} + u^{\mu\mu\mu} + u^{\mu\mu\mu\mu}, \quad (2)$$

where:

$$u^{\mu\mu} = \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r^3} - \frac{3(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r})}{r^5} = \frac{\mu^2}{r^3}(c\gamma_{12} - 3c_1c_2), \quad (3)$$

$$u^{\mu\mu\mu} = \frac{3Q^2}{4r^5}(1 - 5c_1^2 - 5c_2^2 - 15c_1^2c_2^2) + \frac{3Q^2}{4r^5}(2(c\gamma_{12} - 5c_1c_2)^2), \quad (4)$$

$$u^{\mu\mu\mu\mu} = \frac{3\mu Q}{2r^4}c_{12}(1 + 5c_1c_2 - 2c\gamma_{12}), \quad (5)$$

where $c_i = \cos \theta_i$, $s_i = \sin \theta_i$, $c_{ij} = \cos(\theta_i\theta_j)$ and $c\gamma_{ij} = \cos \gamma_{ij} = \mathbf{e}_i \cdot \mathbf{e}_j = \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos(\phi_i - \phi_j)$. The molecular core and the reference framework used to define the pair potential are shown in figure 1. None of the models considered here have a dipole and a quadrupole moment simultaneously. So, the crossed term $u^{\mu\mu\mu}$ in equation (3) given by equation (5) always vanishes.

Monte Carlo simulations were carried out in the canonical ensemble (N , V and T fixed) using 256 parti-

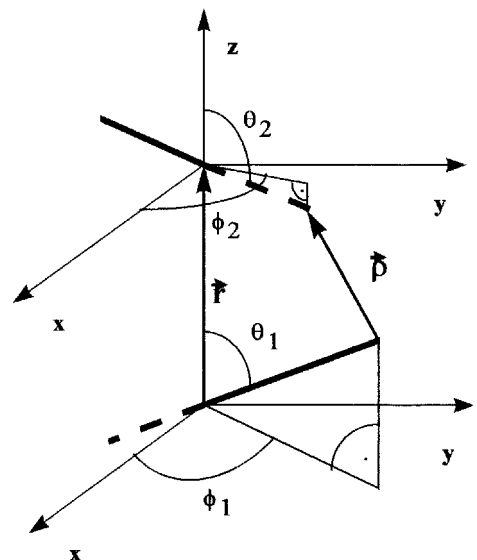


Figure 1. The molecular model considered in this work and the reference framework defining the intermolecular potential.

cles of reduced length $L^* = 0.5233$. The Kihara potential was truncated to the shortest distance, ρ , between molecules of 2.5σ assuming an uniform fluid beyond this distance. Reaction field boundary conditions were used for the dipole interaction and a dielectric constant of $\epsilon_{\text{RF}} = \infty$ was used. Dipole interaction was truncated at a distance between the centres of mass, r , equal to $2.5\sigma + L$. 3000–5000 cycles were performed to reach equilibrium and additionally 3000–5000 more to obtain the averages. A cycle consists of 256 molecular configurations. The thermodynamic quantities directly obtained were the total internal energy, U , the dipole contribution to the total energy, U^μ , and pressure, p . Furthermore, coefficients in the spherical harmonics expansion of the pair correlation function, $g(\mathbf{12})$, were obtained in the same runs and the dielectric constant, ϵ , was estimated from the g_{110} and g_{111} coefficients as:

$$\frac{(\epsilon + 1)(2\epsilon + 1)}{9\epsilon} = y g_K, \quad (6)$$

where g_K is the Kirkwood factor related to these harmonic coefficients by:

$$g_K = 1 + \frac{4n\pi}{3} \int (g_{110} - 2g_{111}) r^2 dr \quad (7)$$

and

$$y = (4n\pi\mu^2/9kT) \quad (8)$$

is the so-called dipole force. The dipole Helmholtz free energy, A^μ , was calculated by thermodynamic integration using the Kirkwood coupling parameter method and the square of the reduced dipole moment, $\mu^{*2} = \mu^2/\epsilon\sigma^3$ as an integration variable:

$$A^\mu = A(\mu^{*2}) - A(0) = \int_0^{\mu^{*2}} \left\langle \left(\frac{\partial U}{\partial \mu^{*2}} \right)_{N, V, T} \right\rangle d\mu^{*2}. \quad (9)$$

Furthermore, we find that the dipole contribution can be well fitted to the following equation:

$$U^\mu / N k_B T = a\mu^{*2} + b(\mu^{*2})^2 \quad (10)$$

and thus, the dipole contribution to the free energy can be explicitly written as:

$$A^\mu / N k_B T = a\mu^{*2} + \frac{1}{2}b(\mu^{*2})^2. \quad (11)$$

Equations totally similar to (9), (10) and (11) can be written for the quadrupole contribution to U and A by substituting μ^{*2} with Q^{*2} , where $Q^{*2} = Q^2/\epsilon\sigma^5$. The non-polar contribution to the free energy was obtained from the improved perturbation theory (IPT) of Vega and Lago [21] which was found accurate enough.

3. Results

Monte Carlo (MC) results for internal energy and compressibility factors of systems interacting through

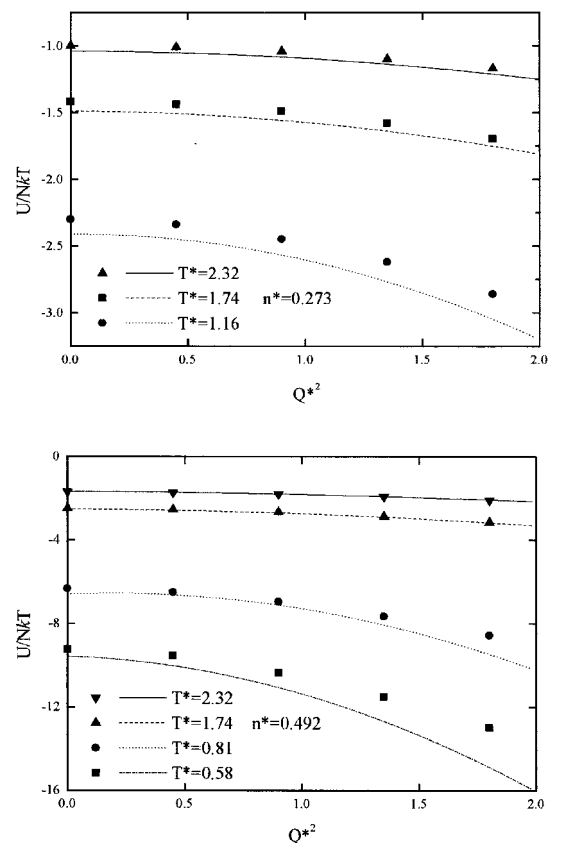


Figure 2. (a) Internal energy as a function of quadrupole moment for a reduced density $n^* = 0.273$ at several temperatures. Discrete symbols are the results of Boublík perturbation theory and lines fit to our MC results. (b) As (a) but for $n^* = 0.492$.

Kihara plus quadrupole potentials are shown in table 1 and in figures 2 and 3. Agreement between simulations and results from the Boublík theory [9] is good specially at low quadrupole and high densities as expected from a perturbation theory. Fitting parameters to the equations (9) and (10) are shown in table 2. It is quite apparent from table 1 that some compressibility factors are negative for high quadrupole and high densities and we discuss this behaviour below. These values were not used to obtain the fitting parameters.

The negative values for the compressibility factor confirm previous observations suggesting the appearance of a solid phase [22] or a highly ordered phase [23] for these thermodynamic states. Our simulations always started from an α -N₂ solid lattice and in spite of performing long runs in these cases the systems with the highest quadrupoles still showed radial distribution functions strongly recalling those of a solid as shown in figure 4. However, these features do not appear at higher temperatures at any quadrupole or density as shown in figure 5. To confirm this point we calculated [16, 24]

Table 1. Comparison between thermodynamic properties of quadrupolar linear Kihara fluids obtained by computer simulation (MC) and the perturbation theory of Boublik (PT).

Q^{*2}	T^*	n^*	MC				PT		
			U/NkT	Z	U^Q/NkT	A^Q/NkT	A^{res}/NkT	U/NkT	Z
0			- 2.41 ₃	0.53 ₇	0	0	- 1.12	- 2.30	0.44
0.45			- 2.45 ₄	0.48 ₈	- 0.04	- 0.03	- 1.15	- 2.34	0.42
0.90	1.16	0.273	- 2.57 ₄	0.40 ₈	- 0.17	- 0.10	- 1.22	- 2.45	0.34
1.35			- 2.76 ₃	0.35 ₈	- 0.37	- 0.20	- 1.32	- 2.62	0.23
1.80			- 3.05 ₅	0.19 ₈	- 0.64	- 0.34	- 1.46	- 2.86	0.07
0			- 1.49 ₃	1.31 ₇	0	0	- 0.24	- 1.42	1.22
0.45			- 1.50 ₃	1.29 ₇	- 0.02	- 0.01	- 0.25	- 1.44	1.21
0.90	1.74	0.273	- 1.56 ₃	1.21 ₇	- 0.08	- 0.05	- 0.29	- 1.49	1.17
1.35			- 1.64 ₃	1.17 ₇	- 0.18	- 0.10	- 0.34	- 1.58	1.11
1.80			- 1.75 ₃	1.12 ₇	- 0.30	- 0.16	- 0.40	- 1.70	1.02
0			- 1.04 ₃	1.66 ₆	0	0	0.16	- 1.00	1.58
0.45			- 1.05 ₃	1.62 ₆	- 0.01	- 0.01	0.15	- 1.01	1.57
0.90	2.32	0.273	- 1.08 ₃	1.61 ₆	- 0.05	- 0.03	0.13	- 1.04	1.55
1.35			- 1.14 ₃	1.58 ₆	- 0.11	- 0.06	0.10	- 1.10	1.51
1.80			- 1.21 ₃	1.63 ₆	- 0.18	- 0.10	0.06	- 1.17	1.46
0			- 9.64 ₇	0.86 ₂₆	0	0	- 5.69	- 9.25	- 0.06
0.45			- 9.97 ₇	0.38 ₃₈	- 0.35	- 0.30	- 5.99	- 9.55	- 0.43
0.90	0.58	0.492	- 10.73 ₁₀	- 0.36 ₂₉	- 1.21	- 0.86	- 6.55	- 10.34	- 1.43
1.35			- 13.14 ₁₀	- 7.97 ₂₉	- 3.21	- 1.69	- 7.38	- 11.51	- 2.93
1.80			- 14.69 ₈	- 10.51 ₂₇	- 4.78	- 2.79	- 8.48	- 12.97	- 4.77
0			- 6.53 ₆	3.37 ₂₅	0	0	- 2.76	- 6.33	2.40
0.45			- 6.72 ₆	3.12 ₂₆	- 0.20	- 0.06	- 2.82	- 6.50	2.19
0.90	0.81	0.492	- 7.18 ₇	2.59 ₂₃	- 0.71	- 0.31	- 3.07	- 6.96	1.62
1.35			- 7.86 ₈	1.75 ₂₄	- 1.46	- 0.73	- 3.49	- 7.66	0.76
1.80			- 9.54 ₁₈	- 2.87 ₄₄	- 2.85	- 1.34	- 4.10	- 8.56	- 0.17
0			- 2.52 ₅	5.69 ₁₈	0	0	0.78	- 2.49	5.08
0.45			- 2.56 ₆	5.64 ₂₀	- 0.06	- 0.04	0.74	- 2.54	5.03
0.90	1.74	0.492	- 2.69 ₆	5.48 ₁₉	- 0.20	- 0.13	0.65	- 2.66	4.87
1.35			- 2.90 ₆	5.22 ₁₉	- 0.43	- 0.25	0.53	- 2.87	4.64
1.80			- 3.16 ₇	4.89 ₁₉	- 0.71	- 0.41	0.37	- 3.14	4.32
0			- 1.67 ₅	5.92 ₁₈	0	0	1.42	- 1.69	5.44
0.45			- 1.70 ₅	5.85 ₁₈	- 0.04	- 0.03	1.39	- 1.72	5.41
0.90	2.32	0.492	- 1.79 ₅	5.74 ₁₇	- 0.13	- 0.08	1.34	- 1.80	5.32
1.35			- 1.91 ₅	5.59 ₁₈	- 0.26	- 0.16	1.26	- 1.92	5.18
1.80			- 2.07 ₆	5.44 ₁₈	- 0.44	- 0.26	1.16	- 2.09	4.98

critical temperatures for $L^* = 0.5233$ and $Q^{*2} = 0, 0.45, 0.9, 1.35$ and 1.8 . The resulting temperatures are $1.020, 1.060, 1.101, 1.141$ and 1.182 , respectively. Moreover, we performed a series of independent MC simulations in the Gibbs ensemble (GEMC) obtaining $T_c = 1.031$ for the non-polar systems in good agreement with our estimations. Values of T_t/T_c , the ratio of the triple point to critical temperatures, is about 0.7 for these elonga-

tions [22] in dumbbells. Kihara rods behave in a similar way to dumbbells and, thus, $T^* = 0.58$ should be well below of the triple point temperature for all the quadrupoles considered here even showing for the highest ones a non-physical behaviour corresponding to negative z values. However, $T^* = 0.81$ should lie below the triple point only for the highest quadrupole and, indeed, this is the only system showing a negative z value. Solid den-

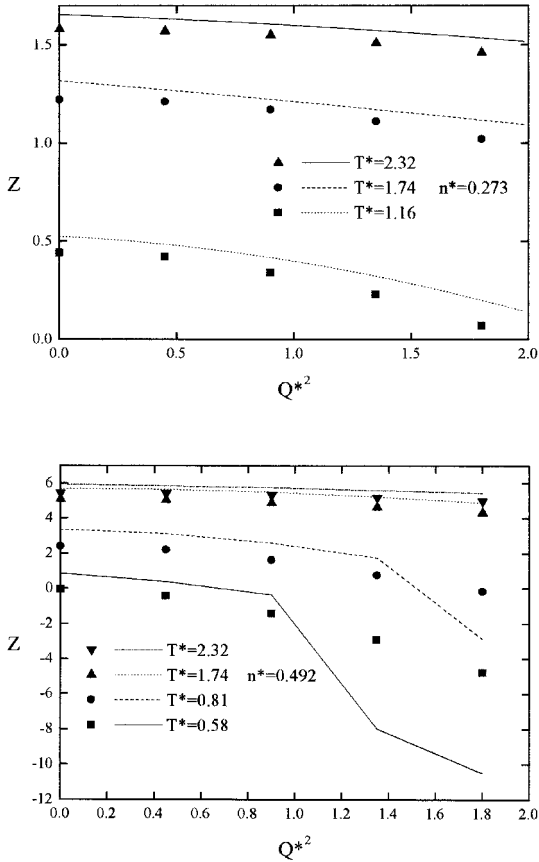


Figure 3. (a) As figure 2(a) but for the compressibility factor.
(b) As (a) but for $n^* = 0.492$.

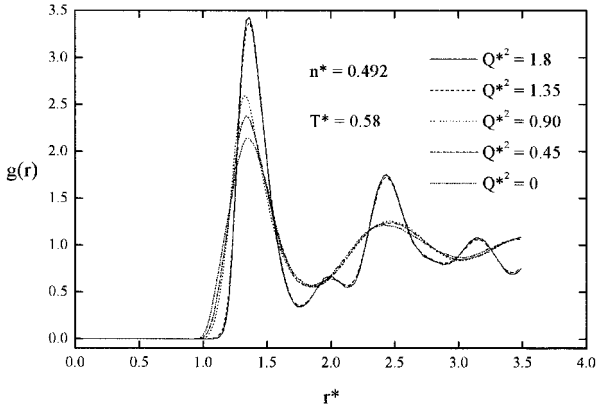


Figure 4. The radial distribution function of several quadrupole systems at $T^* = 0.58$ and $n^* = 0.492$.

sities as a function of temperature are more difficult to estimate but should be about 2.5 times the critical densities, which is about 0.19 for these models, namely 0.493 should correspond to a two phase state for

Table 2. Fitting parameters of equations (10) and (11) of the main text for the internal and Helmholtz energies of quadrupolar linear Kihara fluids as obtained by computer simulation (MC).

Q^{*2}	T^*	n^*	a	b
0				
0.45				
0.90	1.16	0.273	- 0.026	- 0.183
1.35				
1.80				
0				
0.45				
0.90	1.74	0.273	- 0.013	- 0.086
1.35				
1.80				
0				
0.45				
0.90	2.32	0.273	- 0.009	- 0.051
1.35				
1.80				
0				
0.45				
0.90	0.58	0.492	- 0.366	- 1.313
1.35				
1.80				
0				
0.45				
0.90	0.81	0.492	0.066	- 0.903
1.35				
1.80				
0				
0.45				
0.90	1.74	0.492	- 0.057	- 0.189
1.35				
1.80				
0				
0.45				
0.90	2.32	0.492	- 0.041	- 0.113
1.35				
1.80				

higher quadrupoles. All these results agree with former observations[22, 23] showing additional evidence about the phase diagram of linear quadrupole substances.

Some relevant conclusions may also be reached when simulation and theory [9] are compared for dipolar systems as shown in table 3 and figures 6 and 7. Fitting parameters to the internal energy as a function of dipole moments, a and b , are shown in table 4. In this case, a

Table 3. Comparison between thermodynamic properties of dipolar linear Kihara fluids obtained by computer simulation (MC) and the perturbation theory of Boublík (PT).

μ^{*2}	T^*	n^*	MC				PT		
			U/NkT	Z	U^μ/NkT	A^μ/NkT	A^{res}/NkT	U/NkT	Z
0			- 2.41 ₃	0.53 ₇	0	0	- 1.12	- 2.30	0.44
0.84			- 2.54 ₄	0.43 ₈	- 0.12	- 0.14	- 1.26	- 2.42	0.38
1.68	1.16	0.273	- 2.80 ₄	0.33 ₈	- 0.39	- 0.32	- 1.44	- 2.73	0.25
3.35			- 3.61 ₃	0.09 ₈	- 1.17	- 0.80	- 1.92	- 3.65	- 0.08
5.03			- 4.66 ₈	- 0.21 ₈	- 2.18	- 1.45	- 2.57	- 4.78	- 0.36
0			- 1.49 ₃	1.31 ₇	0	0	- 0.24	- 1.42	1.22
0.84			- 1.53 ₃	1.25 ₇	- 0.06	- 0.07	- 0.31	- 1.48	1.19
1.68	1.74	0.273	- 1.68 ₄	1.19 ₇	- 0.20	- 0.16	- 0.40	- 1.63	1.11
3.35			- 2.10 ₄	0.97 ₇	- 0.62	- 0.41	- 0.65	- 2.13	0.89
5.03			- 2.63 ₆	0.75 ₈	- 1.17	- 0.76	- 1.00	- 2.79	0.63
0			- 1.04 ₃	1.66 ₆	0	0	0.16	- 1.00	1.58
0.84			- 1.08 ₃	1.62 ₆	- 0.04	- 0.04	0.12	- 1.03	1.56
1.68	2.32	0.273	- 1.16 ₃	1.59 ₆	- 0.12	- 0.09	0.07	- 1.13	1.51
3.35			- 1.42 ₄	1.45 ₇	- 0.39	- 0.25	- 0.09	- 1.44	1.35
5.03			- 1.77 ₅	1.29 ₆	- 0.76	- 0.47	- 0.31	- 1.88	1.15
0			- 5.60 ₅	0.46 ₁₉	0	0	- 2.95		
0.84			- 5.90 ₆	0.21 ₁₈	- 0.40	- 0.37	- 3.32	- 5.73	0.00
1.68	0.81	0.419	- 6.49 ₆	0.03 ₁₇	- 0.94	- 0.80	- 3.75	- 6.35	- 0.35
3.35			- 8.03 ₈	- 0.76 ₁₈	- 2.42	- 1.87	- 4.22	- 7.84	- 1.02
5.03			- 9.84 ₉	- 1.51 ₂₁	- 4.45	- 3.22	- 6.17	- 9.38	- 1.56
0			- 3.70 ₅	2.15 ₁₆	0	0	- 1.12		
0.84			- 3.87 ₅	2.11 ₁₆	- 0.18	- 0.21	- 1.33	- 3.76	1.70
1.68	1.16	0.419	- 4.23 ₅	1.78 ₁₇	- 0.54	- 0.46	- 1.58	- 4.15	1.46
3.35			- 5.17 ₆	1.32 ₁₇	- 1.53	- 1.11	- 2.23	- 5.16	0.93
5.03			- 6.35 ₇	0.74 ₁₇	- 2.76	- 1.94	- 3.06	- 6.29	0.43
0			- 2.25 ₅	3.24 ₁₄	0	0	0.19		
0.84			- 2.34 ₅	3.18 ₁₄	- 0.09	- 0.14	0.08	- 2.28	2.88
1.68	1.74	0.419	- 2.53 ₅	3.05 ₁₄	- 0.29	- 0.24	- 0.05	- 2.49	2.74
3.35			- 3.07 ₆	2.73 ₁₅	- 0.85	- 0.60	- 0.41	- 3.12	2.37
5.03			- 3.75 ₇	2.38 ₁₆	- 1.57	- 1.07	- 0.88	- 3.86	1.97
0			- 1.54 ₄	3.66 ₁₃	0	0	0.77		
0.84			- 1.59 ₄	3.64 ₁₃	- 0.05	- 0.06	0.71	- 1.56	3.36
1.68	2.32	0.419	- 1.72 ₅	3.56 ₁₄	- 0.19	- 0.13	0.64	- 1.70	3.27
3.35			- 2.08 ₅	3.33 ₁₃	- 0.56	- 0.34	0.43	- 2.12	3.00
5.03			- 2.54 ₆	3.12 ₁₄	- 1.05	- 0.64	0.13	- 2.65	2.69

previous comparison [12] with simulations was made on a system interacting through a two centre Lennard-Jones (2CLJ) and using the following semi-empirical rules to scale the potential parameters [10]:

$$\sigma^K / \sigma^{2\text{CLJ}} = 1 - 0.07(L / \sigma^{2\text{CLJ}}) \cong 0.965, \quad (12)$$

$$\varepsilon^K / \varepsilon^{2\text{CLJ}} = 4 - 5/2(L / \sigma^{2\text{CLJ}}) \cong 2.654, \quad (13)$$

where superscripts K and 2CLJ refer to the parameters for Kihara and two centre Lennard-Jones potentials, respectively.

The conclusions of [12] essentially remain but are now reinforced by our more straightforward comparison. Moreover, critical temperatures may be estimated [17, 24] as $T_c^* = 1.020, 1.072, 1.125, 1.229$ and 1.334 from the lowest to the highest dipole in the table 3.

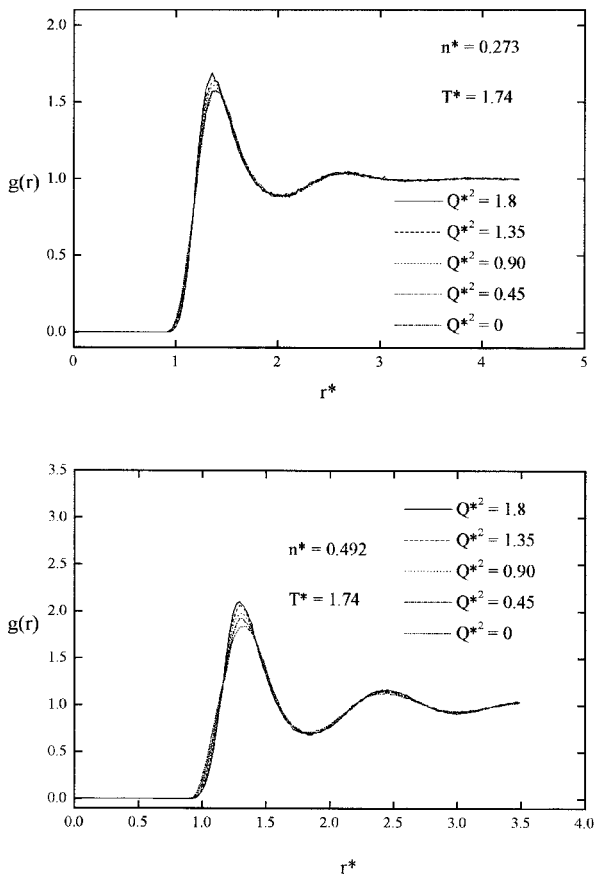


Figure 5. (a) The radial distribution function of several quadrupole systems at $T^* = 1.74$ and $n^* = 0.273$. (b) As for (a) but $n^* = 0.492$.

We are not aware of any estimation of T_t or T_t/T_c for dipole Kihara or dipole dumbbells but our values with negative z suggest that $0.94 > T_t/T_c > 0.66$ for $\mu^{*2} = 3.35$ and $T_t/T_c < 0.87$ for $\mu^{*2} = 5.03$. Therefore, the liquid phase is strongly destabilized for high dipolar systems with respect to non-polar systems [22].

Furthermore, results for the first few spherical harmonics showing the fluid structure are given in figure 8 for the radial distribution function, denoted as $g(r)$ or g_{000} , and in figure 9 for the more physically meaningful combinations of the g_{110} and g_{111} harmonic coefficients:

$$h^{110}(r) = g_{110}(r) - 2g_{111}(r), \quad (14)$$

$$h^{112}(r) = g_{110}(r) + g_{111}(r). \quad (15)$$

The success of the Boublík theory specially for quadrupole molecules is striking and probably comes from the fact that it predicts well the first even coefficients of PCF and we are currently exploring this possibility [25]. These coefficients are the only non-vanishing terms for

Table 4. Fitting parameters, a and b , in equations (10) and (11) of the main text for the internal and Helmholtz energies of dipolar linear Kihara fluids as obtained by computer simulation (MC). y is the dipole force defined by equation (9).

μ^{*2}	T^*	n^*	a	b	y
0					0
0.84					0.276
1.68	1.16	0.273	- 0.141	- 0.059	0.552
3.35					1.101
5.03					1.653
0					0
0.84					0.184
1.68	1.74	0.273	- 0.068	- 0.033	0.368
3.35					0.734
5.03					1.102
0					0
0.84					0.138
1.68	2.32	0.273	- 0.037	- 0.023	0.276
3.35					0.550
5.03					0.826
0					0
0.84					0.607
1.68	0.81	0.419	- 0.397	- 0.097	1.213
3.35					2.420
5.03					3.633
0					0
0.84					0.424
1.68	1.16	0.419	- 0.219	- 0.067	0.847
3.35					1.690
5.03					2.537
0					0
0.84					0.282
1.68	1.74	0.419	- 0.111	- 0.040	0.565
3.35					1.126
5.03					1.691
0					0
0.84					0.212
1.68	2.32	0.419	- 0.064	- 0.029	0.424
3.35					0.845
5.03					1.268

quadrupole systems. Predictions for odd coefficients seem to be worse. In any case, results for dipole systems are not so fair but the estimations are not so sensitive to slight differences in the model as exists between Kihara and 2CLJ. A final but important remark should also be stated: the simulated systems here, used to compare to Boublík's results, correspond to supercritical states in a

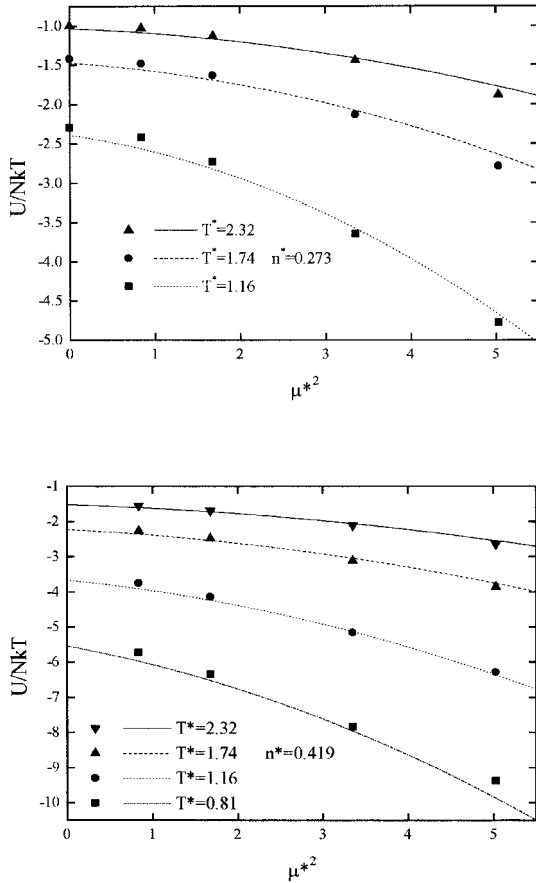


Figure 6. (a) As figure 2(a) but for dipole systems. (b) As figure 2(b) but for dipole systems at $n^* = 0.419$.

number of cases for dipole systems and it is expected that perturbation theories do not work well for these states.

Finally, we also show in table 5 results for the dielectric constant ε as obtained from equation (7) for the highest dipole considered here, $\mu^{*2} = 5.03$. These values should only be considered as a rough estimation to the true value of ε but the main lines of variation with

Table 5. Dielectric constant, ε , of a Kihara linear fluid of $L^* = 0.5233$ and of a Stockmayer fluid, ε_{ST} , at the same dipole force [26], y .

n^*	T^*	y	ε	ε_{ST}
0.273	1.16	1.653	11	15.9
0.273	1.74	1.102	6	8.5
0.273	2.32	0.826	5	5.8
0.419	0.81	3.633	22	110
0.419	1.16	2.537	13	39
0.419	2.32	1.268	6	10.4

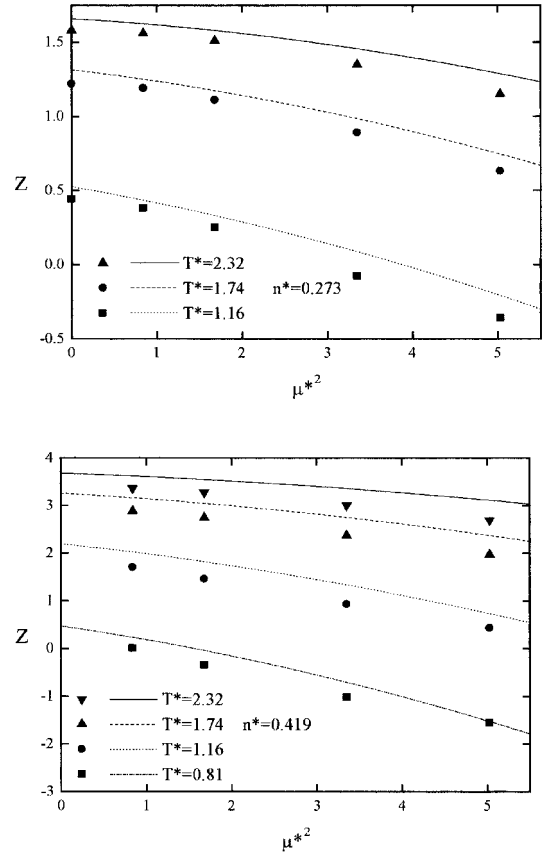


Figure 7. (a) As figure 3(a) but for dipole systems. (b) As figure 2(b) but for dipole systems at $n^* = 0.419$.

density and temperature seem to be clear and so, an estimation of the static dielectric constant can be obtained from the empirical equation:

$$\varepsilon = 5 + 14.1 \exp(-(T^* - 0.88)/0.3861). \quad (16)$$

It is remarkable that the direct dependence of the dielectric constant on density is very weak and it is within the simulation error for the values reported here. The dielectric constant may also be obtained for a Stockmayer fluid from a fitting [26] to the dipole force, y , defined by equation (9). Values obtained from this fitting for the dipole forces considered here are also given in table 5. This comparison consistently shows smaller values of dielectric constant for our anisotropic model at moderate and high dipole forces. It is easy to check using the equation (6) that $g_K > 1$ for all the systems appearing in table 5 indicating a trend of the dipoles to align themselves parallelly but always g_K is less for the anisotropic system indicating that elongation and dipole play an opposite role here. Hansen and McDonald [27] have already pointed out that molecular non-sphericity should have this effect for real molecules

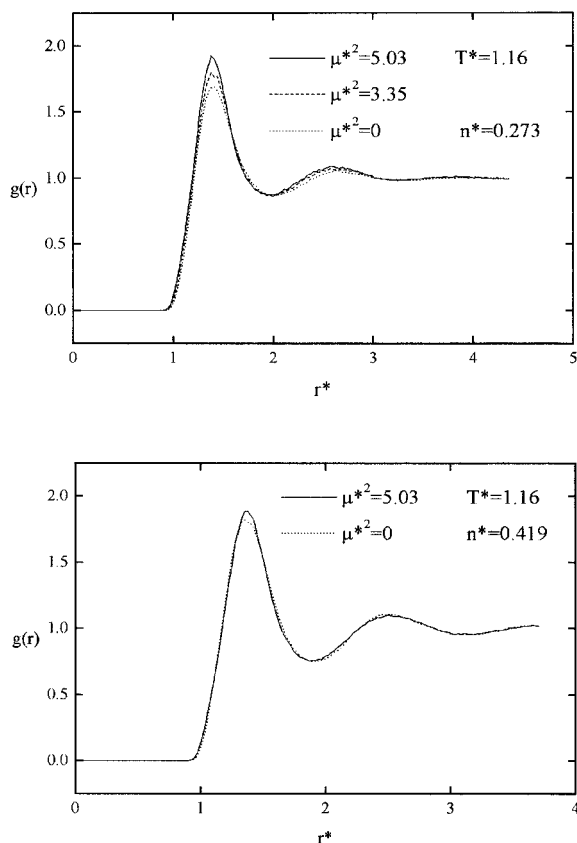


Figure 8. (a) The radial distribution function of several dipole systems at $T^* = 1.16$ and $n^* = 0.273$. (b) As (a) but for $n^* = 0.419$.

because dipole hard spheres [1, 28], as well as Stockmayer models [29, 30], give unrealistic high values of ε for moderate and high dipole moments.

4. Final remarks

The results presented here can cautiously be extended to models of different reduced length and also to include multipole moments, defining the reduced quantities in the way shown in [15–17]. We still are far away from a complete phase diagram for linear molecules with an embedded dipole or quadrupole but all the evidence points to the T_t/T_c ratio as being about 0.7 for values of $L^* \geq 0.5$, in agreement with experimental results for elongated molecules with high quadrupoles such as bromine, CO_2 and acetylene [8]. Strong quadrupole forces reduce the liquid range as pointed out by Vega *et al.* [22] and details to calculate T_t/T_c are given there. The dipole increases the critical temperature and also seems to increase the triple point and the total effect on T_t/T_c is even more apparent than for quadrupole. This is perhaps the reason that weakly dipole liquids such as CO show a T_t/T_c ratio as high as 0.5 instead of 0.3 as

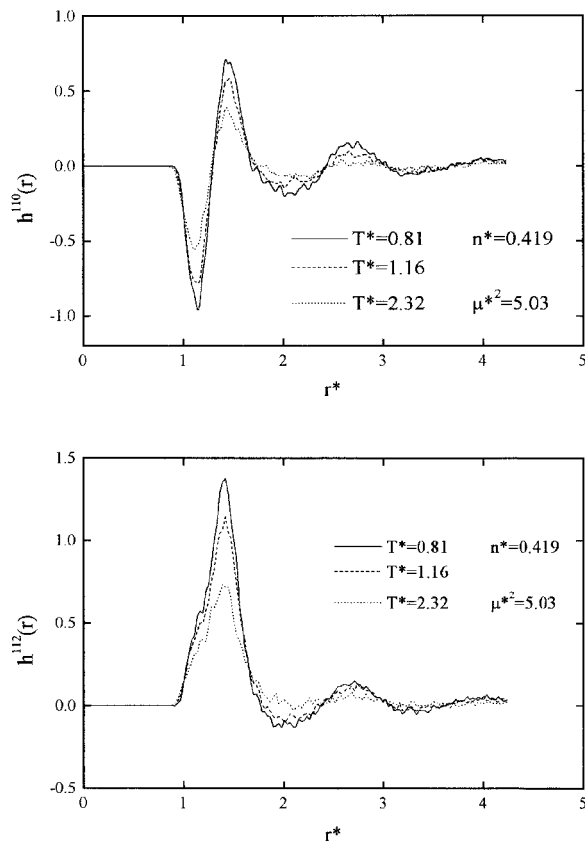


Figure 9. Simulated first few angular coefficients of the pair correlation function of dipole systems at several temperatures for $n^* = 0.419$ and $\mu^{*2} = 5.03$.

weakly quadrupole substances. This variation is sensitive to the dipole moment value and liquids composed of highly dipolar linear molecules seem to become non-existent, namely with an estimated $T_t/T_c > 1$.

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