



Reaction field simulations of the vapor–liquid equilibria of dipolar fluids. Does the reaction field dielectric constant affect the coexistence properties?

Benito Garzón, Santiago Lago *, Carlos Vega

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

Received 4 July 1994; in final form 27 October 1994

Abstract

Vapor–liquid equilibria of two Stockmayer fluids have been obtained by computer simulations in the Gibbs ensemble. The long-range dipolar interactions have been considered within the reaction field geometry. Two different criteria for the reaction field dielectric constant, ϵ_{RF} , have been applied. It is shown that ϵ_{RF} does not significantly affect either the coexistence properties or the structure of coexisting phases for the simulated systems.

1. Introduction

Considerable effort has been devoted to the study of dipolar fluids [1,2]. Thermodynamic perturbation theories [3–7] and integral equations [8–13] have been developed to account for structural and thermodynamic properties of dipolar fluids. On the other hand, several computer simulation experiments have been performed [14–22]. To simulate a dipolar fluid, one must deal with the non-negligible long-range dipolar interactions. Two methods have been designed to treat long-range effects in simulations of polar fluids: the reaction field (RF) approach [23] and the Ewald summation (EW) method [24].

The RF approach replaces particles beyond a cut-off distance by a dielectric continuum. The effect of this continuum is taken into account by including a

new term into the dipolar pair potential. In the EW method, the central simulation box is surrounded by an infinite number of replicas. Then lattice vector sums are taken over spherical shells of an infinite spherical lattice surrounded by a continuum. Neumann and Steinhäuser [15–17] have shown that both methods are equivalent for determining bulk thermodynamic properties when large systems are used.

Since the development by Panagiotopoulos of the Gibbs ensemble Monte Carlo (GEMC) technique [25], which permits a simultaneous simulation of two coexisting phases, the vapor–liquid equilibria (VLE) of some dipolar fluids have been determined by computer simulation [26–30]. In all these works, long-range dipolar interactions were considered by using the EW method. Our aim in this Letter is twofold: to check the validity of the RF approach to simulate the VLE properties of dipolar fluids by using the GEMC technique and to study the influence of the reaction

* Corresponding author.

field dielectric constant upon the coexistence properties of dipolar fluids.

Within the RF geometry, the dipolar pair interaction potential is [16]

$$u_{ij}^{\mu\mu} = \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r^3} - \frac{3(\boldsymbol{\mu}_i \cdot \mathbf{r})(\boldsymbol{\mu}_j \cdot \mathbf{r})}{r^5} - \frac{2(\epsilon_{\text{RF}} - 1)}{2\epsilon_{\text{RF}} + 1} \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r_c^3},$$

$$r < r_c,$$

$$u_{ij}^{\mu\mu} = 0, \quad r \geq r_c, \quad (1)$$

where $\boldsymbol{\mu}_i$ stands for the dipole vector of molecule i , \mathbf{r} is the separation distance vector, $r = |\mathbf{r}|$, r_c is the cut-off distance and ϵ_{RF} the dielectric constant of the continuum. The value of ϵ_{RF} used in computer simulations must be the bulk dielectric constant. Thus, to simulate the coexistence properties of a dipolar fluid by using the GEMC technique with RF, an a priori knowledge of the dielectric constant of each phase is needed. As is well known, the dielectric constant depends on the density, temperature and dipole moment [31], so that a reaction field dielectric constant depending on these properties is desirable. Usually, the $(n-T-\mu)$ -dependence of the dielectric constant of a dipolar fluid model is not known. Thus, to simulate the VLE of such a fluid by using the RF method, the dependence of its dielectric constant must be established in advance. Nevertheless, if the effect of ϵ_{RF} were negligible, it would be possible to perform simulations of the VLE of the dipolar fluid by using a reasonable approximation for ϵ_{RF} . The purpose of this work is to show that ϵ_{RF} does not affect the VLE properties of a dipolar fluid. We have performed GEMC simulations of the VLE of two Stockmayer [14] fluids by using the RF method, with two different criteria for ϵ_{RF} . We have compared the results with the coexistence curve obtained by Smit et al. [26,28] for the same systems, but with the EW approach. Moreover, we have calculated the structure of the gas and liquid coexisting phases at a given temperature for each system, obtained with the two RF criteria.

2. Computer simulations

In a Stockmayer fluid, particles interact through the following pair potential:

$$u_{ij}(r, \omega_i, \omega_j) = u_{ij}^{\text{LJ}}(r) + u_{ij}^{\mu\mu}(r, \omega_i, \omega_j), \quad (2)$$

where $u_{ij}^{\text{LJ}}(r)$ is the Lennard-Jones potential, $u_{ij}^{\mu\mu}(r, \omega_i, \omega_j)$ the dipole–dipole interaction, r is the interparticle distance and ω_i stands for the orientation of molecule i .

On the other hand, Gordon and Goldman [32] have estimated, by fitting several computer simulation data, the dependence of the dielectric constant of the Stockmayer fluid with the *dipolar strength*, y , as a fourth-order polynomial,

$$\epsilon(y) = 1 + 2.932y + 4.210y^2 - 1.323y^3 + 0.6115y^4,$$

$$0 \leq y \leq 3.31, \quad (3)$$

where

$$y = \frac{4\pi n \mu^2}{9k_B T}. \quad (4)$$

y is the dimensionless combination of density, temperature and dipole moment that appears as a *natural* variable in the mean spherical approximation (MSA) theory [2] of dipolar hard spheres. MSA predicts that the dielectric constant of such a system depends on y .

In Eq. (4), n is the number density, μ the dipole moment of each particle, k_B the Boltzmann constant and T the temperature.

Smit and co-workers [26,28] have obtained the coexistence curve of some Stockmayer fluids by using the GEMC technique along with the EW method to account for the long-range dipolar interactions. To check the validity of the RF method for obtaining the VLE of a dipolar fluid and to estimate the influence of ϵ_{RF} onto the coexistence curve, we have performed GEMC simulations of two Stockmayer fluids with the RF method applying two criteria for ϵ_{RF} . The first one, referred hereinafter as method 1, uses the empirical fit of Eq. (3) for the $(n-T-\mu)$ -dependent ϵ_{RF} of each phase. As the density of both phases varies in a GEMC simulation, ϵ_{RF} must be recalculated after each change of density. A second set of coexistence curves of the same systems have been obtained (method 2) with $\epsilon_{\text{RF}}(\text{gas}) = \epsilon_{\text{RF}}(\text{liquid}) = \infty$. As is well known, the dielectric constant of a gas is approximately unity, so that method 2 does not seem to be a good approximation. Nevertheless, if ϵ_{RF} does not affect the coexistence properties of the fluid, the VLE obtained with

this method would be the same as that obtained by method 1.

For all the simulations we have used 512 particles interacting through the Stockmayer potential. The reduced dipole moments considered in this work are $\mu^{*2} = \mu^2 / \epsilon \sigma^3 = 2$ and 4. The coexistence curves of these systems with the EW method have been simulated by Smit and co-workers [26,28]. ϵ and σ are the energy and size parameters of the Lennard-Jones potential, respectively. The pair potential was truncated at a separation distance of $r = 3\sigma$ and the standard long-range corrections were added for the Lennard-Jones part of the interactions [33]. The long-range dipolar interactions were considered within the RF geometry, namely, including a RF term into the pair potential (see Eq. (1)), plus the addition of a RF *self-term* as the long-tail correction [22]. The Gibbs ensemble simulations were performed in cycles, each cycle having three steps: a conventional *NVT* MC cycle in each box, then a volume displacement and finally a

particle exchange between both phases. We used 4000 cycles for equilibration plus 4000 cycles to obtain averages. The estimated errors were obtained from the standard deviations over blocks of 100 cycles.

Critical density, temperature and pressure were obtained by fitting the simulation data to the following expressions:

$$\frac{1}{2}(n_{\ell}^* + n_g^*) = a + bT^*, \quad (5)$$

$$n_{\ell}^* - n_g^* = c(1 - T^*/T_c^*)^\beta, \quad (6)$$

$$\ln P^* = d + e/T^*. \quad (7)$$

n_{ℓ}^* and n_g^* are the liquid and vapor reduced densities ($n^* = n\sigma^3$), $T^* = k_B T / \epsilon$ is the reduced temperature and $P^* = P\sigma^3 / \epsilon$ is the reduced vapor pressure. Eq. (5) is the rectilinear parameters law [34]. In Eq. (6), a critical parameter $\beta = \frac{1}{3}$ is assumed. Eq. (7) is the Clausius–Clapeyron equation for the vapor pressure [35].

The structure of a dipolar fluid is usually estimated

Table 1

Coexistence data for the Stockmayer fluid with $\mu^{*2} = 2$ (upper half) and $\mu^{*2} = 4$ (lower half), obtained by using method 1 described in the text. Results are given in reduced units. $U^* = U/N\epsilon$ is the reduced internal energy. The number in parentheses indicates the uncertainty in units of the last decimal digit: 0.769(11) means 0.769 ± 0.011 . The subscript g refers to gas phase and ℓ to liquid phase

| T^* | n_g^* | P_g^* | U_g^* | n_{ℓ}^* | P_{ℓ}^* | U_{ℓ}^* |
|-------|-------------|-------------|-----------|--------------|--------------|--------------|
| 1.15 | 0.01274(38) | 0.01309(35) | -0.28(2) | 0.769(11) | 0.054(61) | -7.69(11) |
| 1.2 | 0.01947(41) | 0.02003(41) | -0.41(2) | 0.7477(82) | 0.064(49) | -7.40(10) |
| 1.25 | 0.02343(88) | 0.02465(80) | -0.46(3) | 0.7174(79) | 0.072(50) | -7.09(8) |
| 1.3 | 0.0326(17) | 0.0341(18) | -0.60(4) | 0.693(14) | 0.055(42) | -6.81(16) |
| 1.35 | 0.0413(21) | 0.0431(18) | -0.72(5) | 0.661(12) | 0.043(43) | -6.49(11) |
| 1.4 | 0.0563(37) | 0.0567(29) | -0.91(7) | 0.629(17) | 0.059(52) | -6.16(16) |
| 1.45 | 0.0626(53) | 0.0647(38) | -0.96(9) | 0.592(23) | 0.065(46) | -5.81(21) |
| 1.5 | 0.085(12) | 0.0841(84) | -1.23(20) | 0.534(21) | 0.069(29) | -5.29(17) |
| 1.55 | 0.1235(32) | 0.1083(32) | -1.68(5) | 0.532(33) | 0.118(46) | -5.20(29) |
| 1.575 | 0.129(16) | 0.1136(73) | -1.71(18) | 0.484(33) | 0.111(27) | -4.82(25) |
| 1.65 | 0.01917(88) | 0.0253(12) | -0.97(8) | 0.725(18) | 0.12(12) | -10.33(23) |
| 1.7 | 0.0251(20) | 0.0333(19) | -1.14(12) | 0.697(18) | 0.11(11) | -9.93(25) |
| 1.75 | 0.0313(18) | 0.0405(20) | -1.31(11) | 0.669(17) | 0.102(68) | -9.58(20) |
| 1.8 | 0.0379(27) | 0.0491(28) | -1.48(14) | 0.638(24) | 0.103(70) | -9.18(27) |
| 1.85 | 0.0472(21) | 0.0595(24) | -1.68(11) | 0.597(26) | 0.021(96) | -8.68(31) |
| 1.85 | 0.0523(30) | 0.0638(30) | -1.82(11) | 0.625(23) | 0.115(96) | -8.95(26) |
| 1.875 | 0.0583(49) | 0.0689(50) | -1.96(19) | 0.593(33) | 0.112(79) | -8.57(36) |
| 1.9 | 0.0714(36) | 0.0795(44) | -2.28(13) | 0.591(35) | 0.093(81) | -8.56(38) |
| 1.925 | 0.0766(80) | 0.0856(55) | -2.30(26) | 0.557(36) | 0.103(64) | -8.16(38) |
| 1.95 | 0.725(62) | 0.0858(56) | -2.17(18) | 0.513(40) | 0.095(61) | -7.72(39) |
| 1.975 | 0.0846(40) | 0.0969(42) | -2.39(15) | 0.515(33) | 0.124(72) | -7.68(35) |
| 2.0 | 0.0915(75) | 0.1036(60) | -2.51(19) | 0.483(36) | 0.110(52) | -7.32(38) |
| 2.025 | 0.115(10) | 0.1173(94) | -2.99(22) | 0.458(30) | 0.123(55) | -7.07(31) |

through the calculation of the pair correlation function, $g(r, \omega_1, \omega_2)$ [8]. We have considered the three leading terms of the rotational invariant expansion of $h(r, \omega_1, \omega_2) = g(r, \omega_1, \omega_2) - 1$,

$$h(r, \omega_1, \omega_2) = h_{000}(r) + h_{110}(r)\Phi_{110}(\omega_1, \omega_2) + h_{112}(r)\Phi_{112}(\omega_1, \omega_2) + \dots, \quad (8)$$

in which

$$\Phi_{110}(\omega_1, \omega_2) = \mathbf{u}_1 \cdot \mathbf{u}_2 \quad (9)$$

and

$$\Phi_{112}(\omega_1, \omega_2) = \frac{3(\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r})}{r^2} - \mathbf{u}_1 \cdot \mathbf{u}_2, \quad (10)$$

where \mathbf{u}_i is the unit orientation vector of particle i . Furthermore, we have performed NVT MC simulations to calculate the radial distribution function, $g_{000}(r) = h_{000}(r) + 1$, and the two angle dependent projections $h_{110}(r)$ and $h_{112}(r)$ over the coexistence curve at $T^* = 1.4$ for $\mu^{*2} = 2$ and $T^* = 1.95$ for the $\mu^{*2} = 4$ system, using the two criteria for ϵ_{RF} . To obtain accurately the structural properties, we have per-

formed long MC NVT simulations of 5000 cycles for equilibrium plus 45000 cycles to obtain averages.

3. Results and discussion

In Tables 1 and 2 we present the coexistence densities, pressure and energies of Stockmayer fluids of $\mu^{*2} = 2$ and 4, obtained with methods 1 and 2 as described before. In Figs. 1 and 2 we compare these results with the VLE data of the same system given by Smit and co-workers [26,28].

The coexistence densities, shown in Figs. 1a and 2a, obtained by the three methods are essentially the same. Saturation vapor pressures (Figs. 1b and 2b) are also identical, within the statistical accuracy of the simulation data. Even the internal energies of the coexisting phases, shown in Figs. 1c and 2c, are identical.

The three ways of considering the long-range dipolar interactions – namely, EW and the two RF methods of this work – of these systems give the same coexistence properties. This is confirmed by the crit-

Table 2

Coexistence curves for the Stockmayer fluid with $\mu^{*2} = 2$ (upper half) and $\mu^{*2} = 4$ (lower half), obtained by using method 2 described in the text

| T^* | n_g^* | P_g^* | U_g^* | n_l^* | P_l^* | U_l^* |
|-------|-------------|-------------|-----------|------------|-----------|------------|
| 1.15 | 0.0122(10) | 0.01252(98) | -0.31(3) | 0.7613(79) | 0.022(59) | -7.63(10) |
| 1.2 | 0.01727(78) | 0.01736(65) | -0.41(3) | 0.7412(57) | 0.01(5) | -7.39(7) |
| 1.3 | 0.0319(14) | 0.0323(11) | -0.62(4) | 0.6921(93) | 0.021(34) | -6.85(10) |
| 1.4 | 0.0528(53) | 0.0528(41) | -0.89(8) | 0.627(10) | 0.038(38) | -6.19(8) |
| 1.45 | 0.0693(56) | 0.0666(33) | -1.10(9) | 0.601(25) | 0.072(64) | -5.93(23) |
| 1.5 | 0.090(12) | 0.0828(67) | -1.32(16) | 0.556(20) | 0.085(38) | -5.46(17) |
| 1.55 | 0.1256(81) | 0.1070(37) | -1.73(12) | 0.499(54) | 0.114(45) | -4.95(44) |
| 1.575 | 0.1518(65) | 0.1210(38) | -2.01(8) | 0.487(61) | 0.123(49) | -4.85(53) |
| 1.65 | 0.02099(65) | 0.02578(92) | -1.10(6) | 0.715(20) | 0.09(11) | -10.20(25) |
| 1.7 | 0.0251(10) | 0.0311(11) | -1.23(9) | 0.692(17) | 0.08(12) | -9.96(23) |
| 1.75 | 0.0350(16) | 0.0414(18) | -1.52(10) | 0.679(27) | 0.09(10) | -9.75(37) |
| 1.8 | 0.0428(48) | 0.0496(33) | -1.70(23) | 0.637(20) | 0.052(70) | -9.19(24) |
| 1.8 | 0.0393(26) | 0.0474(28) | -1.60(11) | 0.640(24) | 0.07(10) | -9.26(28) |
| 1.85 | 0.0547(20) | 0.0606(31) | -2.01(10) | 0.608(34) | 0.065(65) | -8.86(37) |
| 1.9 | 0.0646(59) | 0.0716(59) | -2.17(21) | 0.574(22) | 0.071(59) | -8.44(24) |
| 1.925 | 0.0771(65) | 0.0806(48) | -2.45(22) | 0.560(31) | 0.081(47) | -8.24(36) |
| 1.95 | 0.0913(64) | 0.0896(46) | -2.71(19) | 0.544(36) | 0.095(64) | -8.04(38) |
| 1.975 | 0.0991(82) | 0.0982(71) | -2.78(21) | 0.499(41) | 0.096(66) | -7.55(42) |
| 2.0 | 0.1273(95) | 0.1097(90) | -3.32(17) | 0.499(36) | 0.112(54) | -7.50(39) |
| 2.025 | 0.126(14) | 0.1146(88) | -3.23(31) | 0.472(29) | 0.122(61) | -7.20(30) |

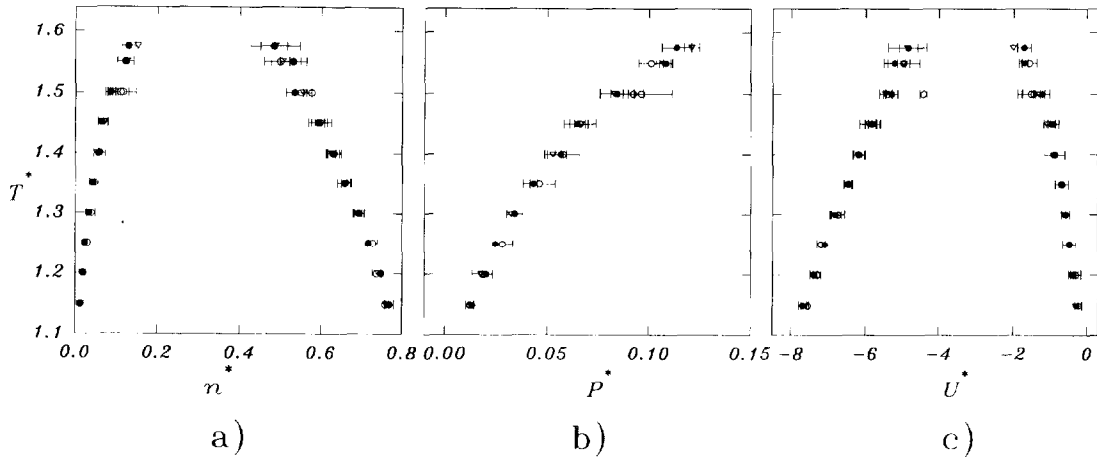


Fig. 1. Vapor-liquid coexistence properties of a Stockmayer fluid with $\mu^{*2} = \mu^2/\epsilon\sigma^3 = 2$, obtained with the EW approach (O) (Ref. [26]) and RF methods 1 (●) and 2 (▽) described in the text. (a) Coexistence densities. (b) Saturation vapor pressure. (c) Internal energies of coexisting phases. The results are given in reduced units, as defined in the text.

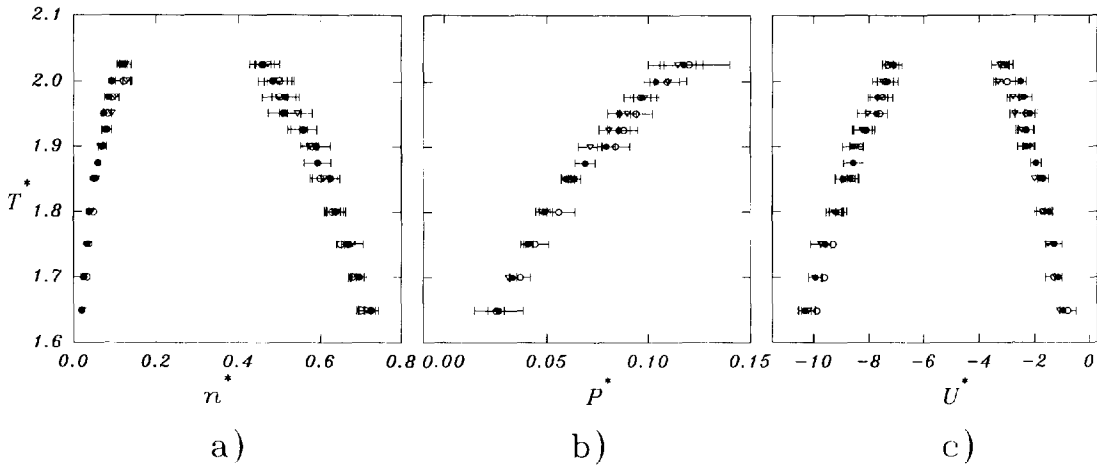


Fig. 2. As Fig. 1, for $\mu^{*2} = 4$. Data obtained with the EW approach from Ref. [28].

Table 3

Reduced critical properties for the Stockmayer fluid of $\mu^{*2} = 2$ and 4, obtained by using the three simulation methods: Ewald summations (EW) (Refs. [26,28,30]) and reaction field (RF) with methods 1 and 2 described in the text

| | EW ^a | RF (method 1) | RF (method 2) | EW ^b | RF (method 1) | RF (method 2) |
|---------|-----------------|---------------|---------------|-----------------|---------------|---------------|
| T_c^* | 1.60(1) | 1.614(46) | 1.615(50) | 2.06(1) | 2.076(37) | 2.071(37) |
| n_c^* | 0.31(1) | 0.298(25) | 0.304(15) | 0.289(8) | 0.278(30) | 0.290(30) |
| P_c^* | | 0.133(33) | 0.137(30) | | 0.136(25) | 0.133(24) |

^a Data obtained from Ref. [26]. ^b Data obtained from Ref. [28].

ical parameters obtained by each method (see Table 3). Critical density, temperature and pressure are – within statistical accuracy – almost identical. The reason why the two RF methods of this work provide almost the same VLE coexistence curve is as follows. Along the liquid branch, values of the dielectric constant are large for the Stockmayer fluids of this work (see Eq. (3)). For large values of ϵ_{RF} the factor $2(\epsilon_{\text{RF}} - 1)/(2\epsilon_{\text{RF}} + 1)$ appearing on the rhs of Eq. (1) is hardly affected by ϵ_{RF} . Therefore, in the liquid branch, the potential of eq. (1) is almost the same for methods 1 and 2. In the gas branch method 1 provides values of ϵ_{RF} close to one whereas method 2 uses $\epsilon_{\text{RF}} = \infty$. However, this difference is of little rele-

vance because of the low densities of the gas.

In Figs. 3 and 4, the $g_{000}(r)$, $h_{110}(r)$ and $h_{112}(r)$ coefficients are given for the gas and liquid coexisting phases at $T^* = 1.4$ for $\mu^{*2} = 2$ and $T^* = 1.95$ for $\mu^{*2} = 4$ as obtained by *NVT* MC simulations by using the two RF methods described before. Within statistical error, the gas and liquid structures obtained by the two methods are practically identical. There is only a slight difference in $h_{110}(r)$ for the liquid phase of the higher dipole moment system: its $h_{110}(r)$ obtained with method 1 is below that obtained with method 2. The area under the curve of $h_{110}(r)$ is proportional to the bulk dielectric constant. In RF simulations, a higher value of ϵ_{RF} provokes a higher bulk dielectric constant [15–17]. This is the effect observed in Fig. 4b: the higher $\epsilon_{\text{RF}} (\infty)$ used in method

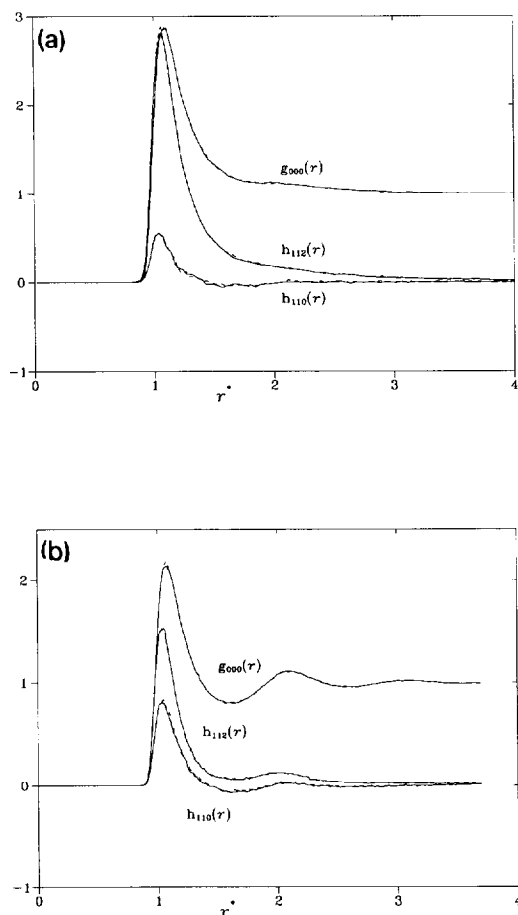


Fig. 3. Structure of the (a) gas and (b) liquid coexisting phases of the Stockmayer fluid with $\mu^{*2} = 2$ at $T^* = 1.4$ obtained by *NVT* MC computer simulations using the RF methods 1 (—) and 2 (---) described in the text.

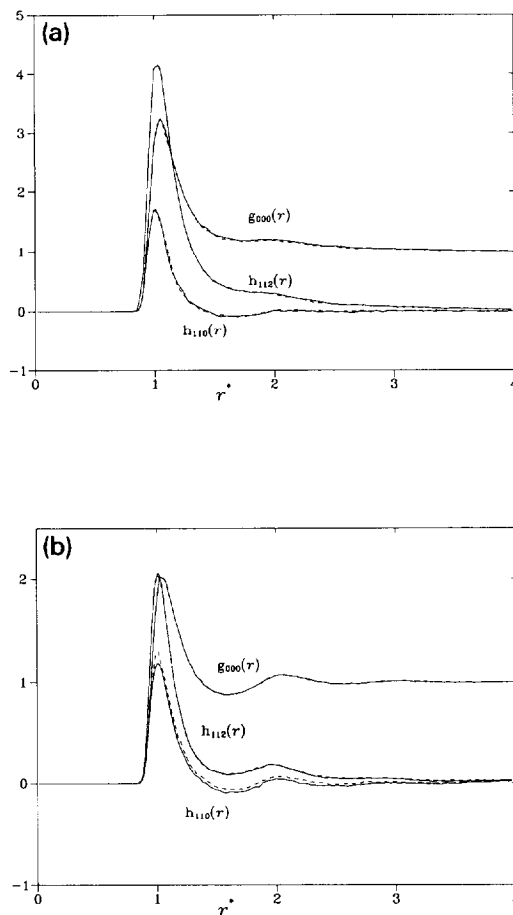


Fig. 4. As Fig. 3, for $\mu^{*2} = 4$ at $T^* = 1.95$.

2 provokes its $h_{110}(r)$ to be above the $h_{110}(r)$ obtained with method 1.

Thus, we can conclude that the RF approach is as good as the EW method for considering the long-range dipolar interactions in GEMC simulations of the VLE of Stockmayer fluids. Moreover, we have shown that the choice $\epsilon = \infty$ (method 2) for the reaction field dielectric constant, ϵ_{RF} , does not affect either the VLE or the structure of the coexisting phases when compared with the more rigorous method 1. This will occur whenever high values of the dielectric constant are found in the liquid branch of the model under consideration. In that case, the answer raised in the title is no, provided that a high value of ϵ_{RF} is used.

The dependence of the dielectric constant of a dipolar fluid on temperature, density and dipole moment is usually unknown. As the RF method is the fastest way of considering long-range dipolar interactions in computer simulations and – at least for the Stockmayer fluids of this work – the use of an arbitrarily high ϵ_{RF} does not affect the coexistence properties, we propose that the RF method 2 of this work can confidently be used to obtain the VLE of a dipolar fluid by computer simulation.

Acknowledgement

This work was financially supported by project No. PB91-0364 of the Spanish DGICYT (Dirección General de Investigación Científica y Técnica). One of us (BG) is grateful for a grant from the Universidad Complutense de Madrid for preparing his Ph.D. Thesis.

References

- [1] J.P. Hansen and I.R. McDonald, *Theory of simple liquids* (Academic Press, New York, 1986).
- [2] C.G. Gray and K.E. Gubbins, *Theory of molecular fluids* (Clarendon Press, Oxford, 1984).
- [3] J.A. Pople, *Proc. Roy. Soc. London A* 221 (1954) 498.
- [4] K.E. Gubbins and C.G. Gray, *Mol. Phys.* 23 (1972) 187.
- [5] G. Stell, J.C. Rasaiah and H. Narang, *Mol. Phys.* 23 (1972) 993.
- [6] M. Lupkowsky and P.A. Monson, *Mol. Phys.* 67 (1989) 53.
- [7] T. Boublík, *Mol. Phys.* 76 (1992) 327.
- [8] G. Stell, G.N. Patey and J.S. Hoye, *Advan. Chem. Phys.* 38 (1981) 183.
- [9] P.H. Fries and G.N. Patey, *J. Chem. Phys.* 82 (1985) 429.
- [10] L.L. Lee, P.H. Fries and G.N. Patey, *Mol. Phys.* 55 (1985) 751.
- [11] F. Lado, M. Lombardero, E. Enciso, S. Lago and J.L.F. Abascal, *J. Chem. Phys.* 85 (1986) 2916.
- [12] M. Lombardero, F. Lado, E. Enciso, S. Lago and J.L.F. Abascal, *An. Fis. A* 84 (1988) 151.
- [13] A.L. Nichols III and D.F. Calef, *Mol. Phys.* 71 (1990) 269.
- [14] D.J. Adams, E.M. Adams and G.J. Hills, *Mol. Phys.* 38 (1979) 387.
- [15] M. Neumann and O. Steinhauser, *Chem. Phys. Letters* 95 (1983) 417.
- [16] M. Neumann, *Mol. Phys.* 50 (1983) 841.
- [17] M. Neumann, O. Steinhauser and G.S. Pawley, *Mol. Phys.* 52 (1984) 97.
- [18] S.W. de Leeuw and N. Quirke, *J. Chem. Phys.* 81 (1984) 880.
- [19] S.W. de Leeuw, J.W. Perram and E.R. Smith, *Ann. Rev. Phys. Chem.* 37 (1986) 245.
- [20] E. Lomba, M. Lombardero and J.L.F. Abascal, *Mol. Phys.* 68 (1989) 1067.
- [21] C. Vega, B. Saager and J. Fischer, *Mol. Phys.* 68 (1989) 1079.
- [22] B. Saager, J. Fischer and M. Neumann, *Mol. Simul.* 6 (1991) 27.
- [23] J.A. Barker and R.O. Watts, *Mol. Phys.* 26 (1973) 789.
- [24] S.W. de Leeuw, J.W. Perram and E.R. Smith, *Proc. Roy. Soc. London A* 373 (1980) 27.
- [25] A.Z. Panagiotopoulos, *Mol. Phys.* 61 (1978) 813.
- [26] B. Smit, C.P. Williams, E.M. Hendriks and S.W. de Leeuw, *Mol. Phys.* 68 (1989) 765.
- [27] J.J. de Pablo, J.M. Prausnitz, H.J. Strauch and P.T. Cummings, *J. Chem. Phys.* 93 (1990) 7355; H.J. Strauch and P.T. Cummings, *J. Chem. Phys.* 96 (1992) 864.
- [28] M.E. van Leeuwen, B. Smit and E.M. Hendriks, *Mol. Phys.* 78 (1993) 271.
- [29] G.S. Dubey, S.F. O'Shea and P.A. Monson, *Mol. Phys.* 80 (1993) 997.
- [30] M.E. van Leeuwen and B. Smit, *Phys. Rev. Letters* 71 (1993) 3991.
- [31] C.J.F. Böttcher, *Theory of electric polarization* (Elsevier, Amsterdam, 1973).
- [32] H. Gordon and S. Goldman, *Mol. Simul.* 2 (1989) 177.
- [33] M.P. Allen and D.J. Tildesley, *Computer simulations of liquids* (Clarendon Press, Oxford, 1987).
- [34] E.A. Guggenheim, *J. Chem. Phys.* 13 (1945) 253.
- [35] R.C. Reid, J.M. Prausnitz and B.E. Poling, *The properties of gases and liquids* (McGraw Hill, New York, 1986).