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Vapor–Liquid Equilibrium and Structure of Methyl Iodide Liquid

F. F. Martins Freitas and Fernando M. S. Silva Fernandes*

Department of Chemistry and CECUL, Faculty of Sciences, University of Lisboa, Rua Ernesto de Vasconcelos, Bloco C1, Piso 5, 1700 Lisboa, Portugal

B. J. Costa Cabral

Department of Chemistry and CFMC, Faculty of Sciences, University of Lisboa, Av. Prof. Gama Pinto, 2, 1699 Lisboa, Portugal

Thermal, structural, and vapor–liquid equilibrium properties for a site–site potential model of methyl iodide have been studied using NPT and Gibbs ensemble Monte Carlo simulations. Densities and enthalpies of vaporization are in very good agreement with experiment over a wide range of thermodynamic conditions. The structure reflects competition between antiparallel and linear dimers and suggests that dipolar interactions play an important role in liquid methyl iodide. The critical properties have been estimated by fitting the Gibbs ensemble Monte Carlo results to the laws of rectilinear diameters and order parameter scaling. The estimated values were $T_c = 548.6$ K and $\varrho_c = 0.735$ g cm^{-3}, in good agreement with the experimental values 528 K and 0.747 g cm^{-3}, respectively. The influence of the Coulombic long-range corrections on the vapor–liquid coexistence and critical properties has been analyzed by performing simulations with and without Ewald sums. In order to discuss the importance of the Coulombic interactions, a site–site Lennard-Jones system has also been analyzed.

1. Introduction

Computer simulation studies of the phase equilibria of molecular systems are very important for the understanding of molecular interactions and phase transitions. The correct description of phase coexistence and interfacial properties is a serious test for models and theories of interacting molecular systems.

Until recently, simulational studies of phase equilibria were a very complex task, requiring the evaluation of the chemical potential while searching for the conditions of coexistence. They were based on different approaches as thermodynamic integration,[1] grand canonical Monte Carlo,[2,3] probability ratio,[4] and particle insertion methods.[5,6]

The major thrust in direct simulation of phase equilibria has been the introduction of the Gibbs ensemble (GE) Monte Carlo method by Panagiotopoulos[7] and Panagiotopoulos et al.[8] The method enables the direct calculation of phase coexistence properties of pure components and mixtures, without need for determining or specifying the chemical potential. Since then, the method has successfully been applied to different systems ranging from simple systems to polymers and has been the subject of a detailed review by Panagiotopoulos.[9] Recently, the method has also been applied to reactive systems.[10] The main limitation of the GE method is the poor convergence of the averages when dealing with situations where the exchange of particles become difficult and the equilibrium between phases is very slowly attained. Cavity bias methods[11] or configurational bias methods[12–14] may be useful in extending the range of applicability. Furthermore, the introduction of methods for the direct determination of phase equilibria without exchange of particles[15,16] seems promising.

The recent applications of the GE method to study the vapor–liquid coexistence of argon with nonadditive potentials[17] and

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TABLE 1: Thermal Properties of Liquid Methyl Iodide

T/K	240	260	273	303	315
ϱ/g cm^{-3} ^{a}	2.44	2.38	2.35	2.26	2.22
			(2.33)	(2.26)	(2.23)
ΔH_v/kJ mol^{-1} ^{b}	30.6	29.7	29.3	28.5	27.6
	(30.6)	(29.7)	(29.3)	(28.1)	(27.2)

^{a} Experimental values in parentheses.[34] ^{b} Experimental values in parentheses.[35]

of methyl chloride[18] reflect our interest to simulate realistic models for molecular systems in order to compare the results with experimental data. In this article we present thermal and structural properties of liquid methyl iodide, obtained by the NPT Monte Carlo, and its vapor–liquid and critical properties, obtained by GE Monte Carlo, using a site–site potential model. This system is important for two main reasons. First, until recently and to our knowledge, the only simulations of liquid methyl iodide were carried out by Evans and Evans.[19,20] Their results, however, are not in good agreement with experiment. Recently, we have performed[21] molecular dynamics simulations of this system using a site–site potential model. The calculated dynamical properties are in very good agreement with experimental results. Second, it seems that theoretical and experimental results of the phase equilibrium of methyl iodide are very scarce.

The main purpose of this work is (i) to check the ability of the potential model used in our previous work[21] to reproduce the thermal, vapor–liquid, and critical properties of methyl iodide and (ii) to analyze the influence of the Coulombic long-range corrections and the importance of the Coulombic interactions on the vapor–liquid and critical properties.

In the next section we present the potential model and the computational details. The results are shown and discussed in section 3. Finally, section 4 contains the conclusions of this work.

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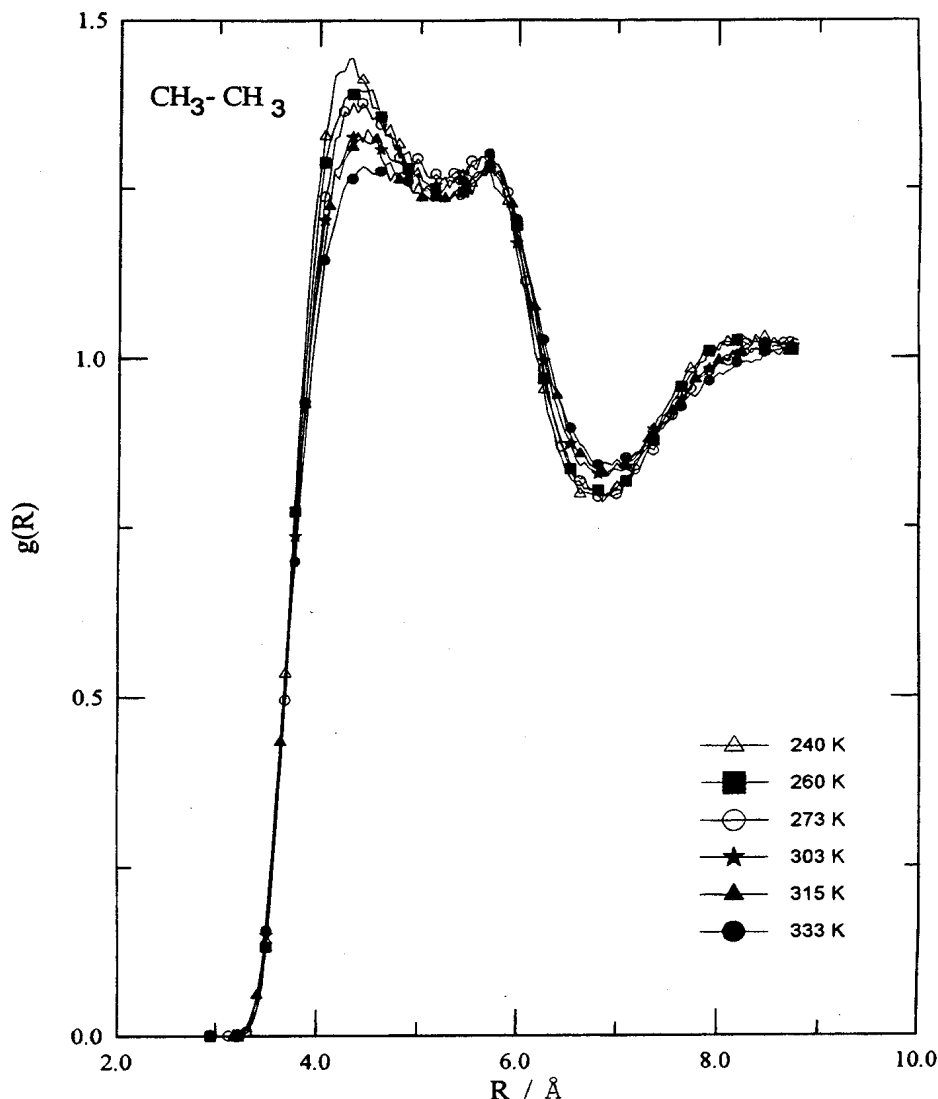
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Figure 1. Site−site distribution functions for CH_3-CH_3.

2. Potential Model and Computational Details

Our model for CH_3I consists of a CH_3 pseudoatom and of an iodine atom separated by 2.16 Å, which is the experimental bond length. The interaction between two CH_3I molecules A and B is described by

$$U_{AB} = \sum_{i \in A} \sum_{j \in B} \epsilon_{ij} [(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6 + q_i q_j/r_{ij}]$$

The parameters for the CH_3 pseudoatom are the same as from other previous studies on molecular liquids, as for example CH_3-Cl.[22] The parameters for iodine have been based on ab initio calculations for the methyl iodide dimer and fitting to liquid state properties.[21] As referred to above, recent molecular dynamics calculations using this set of parameters predicted dynamic properties in very good agreement with experiment.[21] The set of parameters for the site−site Lennard-Jones plus charge distribution interactions was $\sigma_{CH_3} = 3.77$ Å, $\sigma_I = 3.83$ Å, $\epsilon_{CH_3} = 1.6523 \times 10^{-21}$ J, $\epsilon_I = 4.1576 \times 10^{-21}$ J, $q_{CH_3} = 4.0055 \times 10^{-20}$, and $q_I = -4.0055 \times 10^{-20}$ C.

Although our intermolecular potential is an effective pairwise additive site−site model parametrized to reproduce experimental densities and vaporization enthalpies of the liquid, when we analyze the dimers of methyl iodide it appears that the

perpendicular and the linear dimers with methyl approaching iodide are the most energetically favored relative configurations. The positions of the energy minima are 3.55 Å (antiparallel) and 6.2 Å (linear). This is in agreement with the results of Huang and Guo for dimers of methyl iodide.[23] As it has been remarked by these authors, although the relative contribution of the dipolar interaction to the total energy is small compared to the dispersion-like interactions, the interactions between dipoles contribute significantly to the formation of antiparallel dimers. Thus, the presence of antiparallel dimers in condensed phases can be anticipated as reflecting the importance of Coulombic interactions to the orientational ordering in methyl iodide.

The NPT Monte Carlo simulations for the liquid were carried out with 500 molecules in a cube with periodic boundary conditions. The initial configuration for the first simulation of liquid methyl iodide (at 315 K) has been generated from the site coordinates of a simulation of liquid methyl chloride.[24] The site coordinates have been rescaled to reproduce the experimental C−I bond length in methyl iodide (2.16 Å). For the other temperatures, thermalized configurations of methyl iodide have been used. Equilibration runs of 2000−3000 Monte Carlo cycles have been followed by production runs with 4000−6000 cycles.
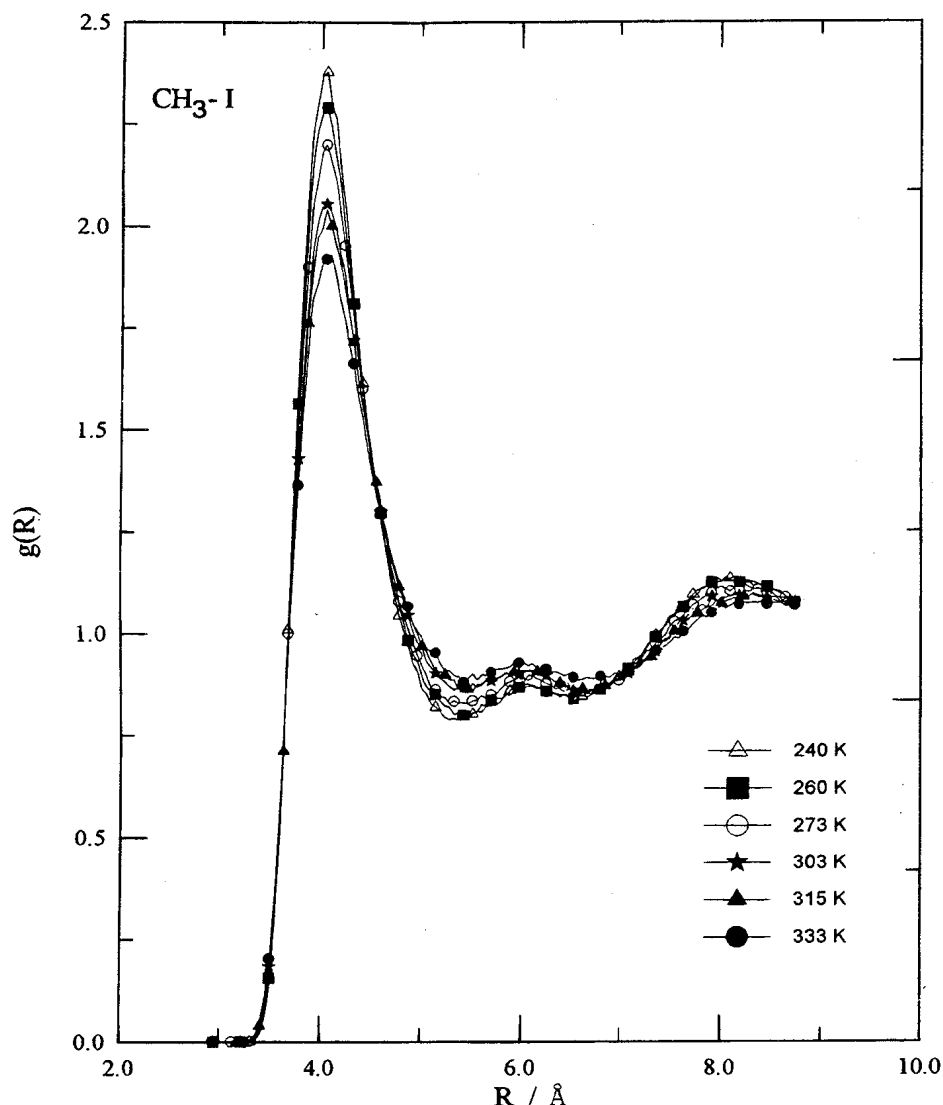
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Figure 2. Site—site distribution functions for CH_3—I.

Our NPT Monte Carlo simulations are in perfect agreement with NPT molecular dynamics simulations of liquid methyl iodide.[21] Comparison with molecular dynamics or biased Monte Carlo procedures is very important in situations where standard Metropolis sampling may not be adequate, as, for example, in the simulations of adsorption processes in a surface[23] or interfaces.[25]

All the interactions have been truncated within a sphere of ~15 Å. It is well-known that the thermal properties of the pure liquid are not, in general, significantly sensitive to long-range Coulombic corrections while these corrections are essential to describe dynamical properties.[24] The importance of those corrections to study phase equilibria properties also merits attention as thoroughly explained by Smit.[26] In this sense, Gibbs ensemble Monte Carlo simulations have been carried out, and the long-range electrostatic interactions have been taken into account using an accurate procedure proposed by Adams and Dubey[27] to perform Ewald sums. In addition, we have also carried out simulations with truncated Coulombic interactions, i.e., without Ewald sums and also without charges, which corresponds to a site—site Lennard-Jones system.

Extensive computational details on the Gibbs ensemble and on its theory can be found in the refs 7—9, 26, 28, and 29. As such, we only present a very short outline of our computations.

Cubic periodic boundary conditions were used with a total number of 512 molecules. For each thermodynamic state studied, the initial configurations were taken as fcc lattices, and the initial densities were chosen according to the experimental values. Equilibration runs with 2000—4000 Monte Carlo cycles were always followed by production runs with 6000—10 000 cycles. The number of attempts per cycle to insert a particle was adjusted in order to obtain acceptance rates between 0.2% and 8%. Cumulative averages of densities and configurational energies were monitored, and no significant drifts were observed after the system has reached equilibrium and for the duration of the production runs. The chemical potentials were estimated using the Widom method.

In GE simulations special care must be taken in order to guarantee that the system is not trapped in local minima. In this sense and in order to check out our computer programs, we have first studied the vapor—liquid equilibrium of chlorine using the Lennard-Jones site—site model of Singer et al.[30] This model was used by Tildesley[31] to successfully reproduce the experimental vapor—liquid equilibrium curve of chlorine. Our results are also in excellent agreement with the experimental ones. Second, we have taken into account the two possible ways[26] of making the Monte Carlo steps (particle displacements, volume change, and particle exchange): either sequentially or

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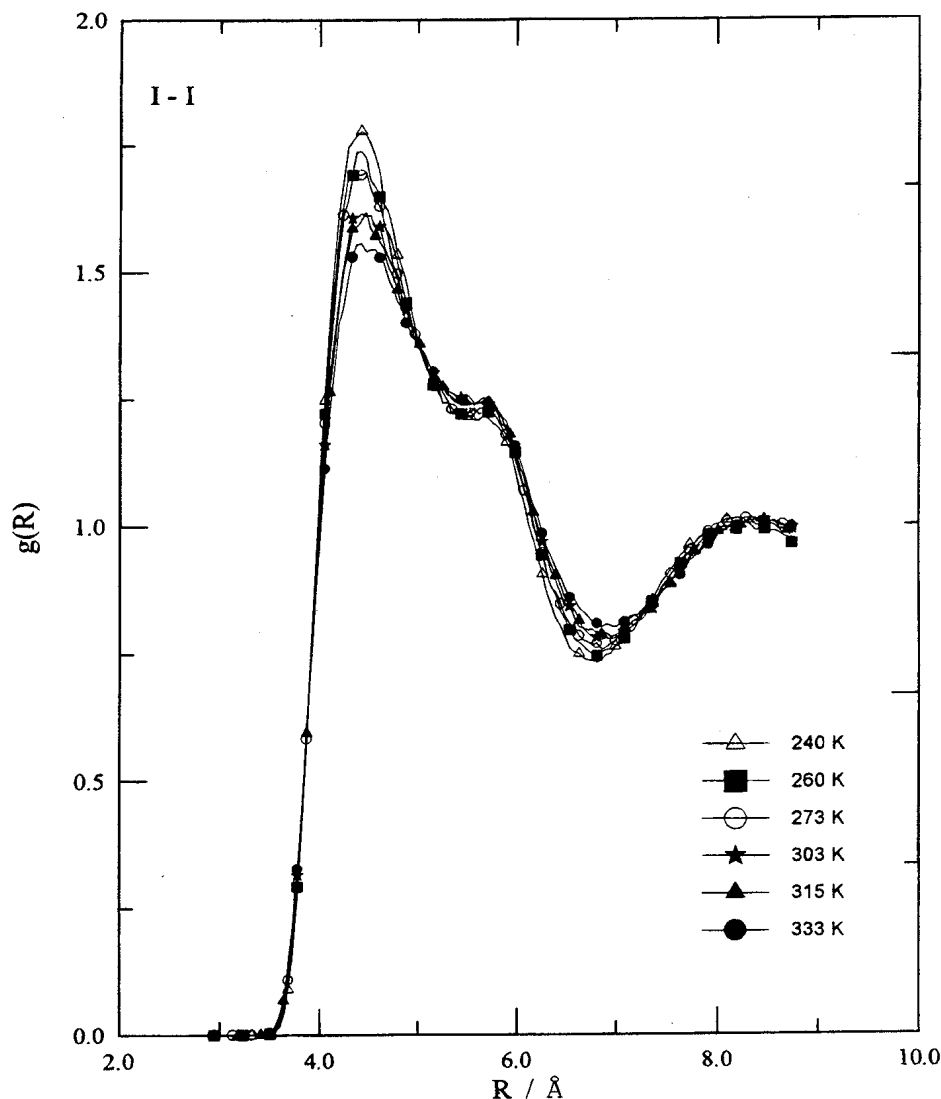*J. Phys. Chem., Vol. 99, No. 14, 1995* **5183**

Figure 3. Site—site distribution functions for I—I.

randomly. As these procedures are not theoretically equivalent, this is a serious test regarding the ergodicity of the system. The results from the two procedures for methyl iodide were totally equivalent.

In order to estimate the critical properties, the vapor—liquid densities were fitted to the *law of rectilinear diameters*[32]

$$\frac{\varrho_L + \varrho_V}{2} = \varrho_C + A\left(1 - \frac{T}{T_C}\right)$$

and to the *law of order parameter scaling*[32]

$$\frac{\varrho_L - \varrho_V}{2} = B\left(1 - \frac{T}{T_C}\right)^\beta$$

where β is the critical exponent taken as 0.313 from the 3-D Ising model.[33]

The calculations were carried out in the C3410 CONVEX, IBM/RISC 6000/590, and DIGITAL/ALPHA/3000/4000.

3. Results and Discussion

3.1. Thermal Properties. Densities and enthalpies of vaporization are reported in Table 1. Our model has been parameterized to reproduce the density and vaporization energy

at 315 K.[21] Nevertheless, a good agreement between theory and experiment can be observed for a wide set of thermodynamic states in the liquid phase, as is illustrated in Table 1. For the density, the deviations from experimental values[34] are less than 2%. We have also verified that our predicted densities at high pressures are in good agreement with experiment. Thus, at 2000 atm our result is 2.6 g cm⁻³, which is also the experimental value.[34]

The experimental enthalpy of vaporization at 315 K is 27.2 kJ mol⁻¹.[35] For the other temperatures they have been estimated by the Watson relation[35] $\Delta H_{\nu_1} = \Delta H_{\nu_2}((1 - T_{\nu_1})/(1 - T_{\nu_2}))^n$, where the subscripts 1 and 2 refer to temperatures 1 and 2 and n has been chosen as 0.38.[35] The good agreement between theoretical and experimental data for the densities and vaporization energies suggests that our model provides a good description of the thermal properties of liquid methyl iodide.

3.2. Structure. The site—site radial distribution functions for CH₃I are presented in Figures 1—3. They reflect the energetic competition of the interactions between dimers and allow a global view of the correlations between translational and orientational freedom in the liquid phase. We are not aware of experimental data on the structure of liquid methyl iodide.

(a) CH₃—I. They are characterized by maxima at ∼4.2 Å. These maxima are related to the presence of antiparallel dimers.

TABLE 2: Vapor—Liquid Coexistence Data for the Charged Model with and without Ewald Sum (EW and WEW), Lennard-Jones Model (LJ) and Experimental Results (EXP); Densities (ϱ), Internal Energies (U), and Reduced Chemical Potentials (μ)[a]

T/K		$\varrho_L/g\ cm^{-3}$	$\varrho_V/g\ cm^{-3}$	$U_L/kJ\ mol^{-1}$	$U_V/kJ\ mol^{-1}$	μ_L	μ_V
380	EXP	1.986	0.026				
	EW	2.080(27)	0.030(4)	−23.37(34)	−0.69(23)	−6.47(39)	−6.53(19)
	WEW	2.052(28)	0.028(2)	−22.87(32)	−0.62(20)	−6.63(40)	−6.61(20)
	LJ	1.909(41)	0.088(1)	−18.10(44)	−1.29(14)	−6.18(37)	−5.37(16)
410	EXP	1.865	0.048				
	EW	1.959(32)	0.040(2)	−21.73(39)	−0.81(19)	−6.46(39)	−6.67(20)
	WEW	1.947(35)	0.048(3)	−21.43(42)	−0.96(20)	−6.16(37)	−6.48(19)
	LJ	1.773(52)	0.098(1)	−16.62(51)	−1.33(13)	−5.48(33)	−5.66(17)
420	EXP	1.822	0.057				
	LJ	1.740(55)	0.092(1)	−16.25(54)	−1.22(12)	−6.04(36)	−5.82(17)
430	EXP	1.777	0.069				
	EW	1.885(37)	0.054(3)	−20.79(43)	−1.04(19)	−6.07(36)	−6.62(20)
	WEW	1.859(43)	0.061(4)	−20.31(47)	−1.15(19)	−7.41(44)	−6.50(19)
	LJ	1.688(54)	0.102(2)	−15.68(54)	−1.31(12)	−5.34(32)	−5.82(17)
440	EXP	1.731	0.082				
	LJ	1.575(60)	0.090(1)	−14.69(57)	−1.13(11)	−5.72(34)	−6.06(18)
450	EXP	1.683	0.097				
	EW	1.799(51)	0.073(5)	−19.68(59)	−1.31(19)	−6.31(38)	−6.56(20)
	WEW	1.761(49)	0.087(1)	−19.10(56)	−1.55(17)	−6.43(38)	−6.38(19)
	LJ	1.511(89)	0.096(2)	−14.08(74)	−1.19(11)	−5.92(35)	−6.14(18)
460	EXP	1.632	0.115				
	EW	1.781(47)	0.092(2)	−19.39(56)	−1.61(17)	−5.87(35)	−6.41(19)
	WEW	1.718(56)	0.090(1)	−18.59(59)	−1.57(17)	−6.54(39)	−6.47(19)
	LJ	1.469(104)	0.093(1)	−13.66(86)	−1.13(11)	−6.41(38)	−6.22(19)
480	EXP	1.521	0.160				
	EW	1.675(52)	0.099(3)	−18.17(59)	−1.65(17)	−6.73(40)	−6.59(20)
	WEW	1.614(72)	0.098(2)	−17.34(75)	−1.62(16)	−6.89(41)	−6.65(20)
490	EXP	1.459	0.189				
	EW	1.624(75)	0.113(1)	−17.59(80)	−1.83(16)	−6.31(38)	−6.52(19)
	WEW	1.521(69)	0.115(3)	−16.28(73)	−1.87(17)	−6.18(37)	−6.57(20)
500	EXP	1.390	0.224				
	EW	1.441(111)	0.118(2)	−15.75(1.06)	−1.86(15)	−6.74(40)	−6.60(20)

[a] The vapor and liquid phases are labeled V and L, respectively; the numbers in parentheses are the estimated root mean square (standard deviations over the entire production runs) of the last digit(s), so 2.080(27) means 2.080 ± 0.027.

The broad shoulder at ~5.8 to ~6.2 Å suggests some orientational freedom between antiparallel and linear configurations which is reduced at lower temperatures.

At lower temperatures, the first maxima (assigned to the presence of antiparallel dimers) are clearly reinforced. This reflects the link between the interaction model, which predicts the presence of energetically favored antiparallel dimers, and the positional and orientational correlations, which determine the structure in condensed phases. This picture is in agreement with an X-ray diffraction study of the methyl iodide crystal structure by Kawaguchi et al.,[36] which pointed out the presence of antiparallel dimers as the dominant structural feature in the crystal. The positions of the maxima and of the closest approach distance are almost independent of the temperature, suggesting that the orientational order plays an important role in the structure of liquid methyl iodide.

(b) CH₃—CH₃ and I—I. These radial distribution functions are both bimodal and present some similarities. Thus, the two maxima at ~4.5 and ~6.0 Å are related respectively with the presence of antiparallel and linear configurations. The orientational freedom between these configurations is reflected by the presence of a plateau between the two maxima. The pronounced height of the first maxima of the I—I radial distribution functions at low temperatures is essentially related to antiparallel dimers, favored by Coulombic interactions, suggesting that dipolar interactions play an important role in liquid methyl iodide.

3.3. Vapor—Liquid Equilibrium and Critical Properties.
It is well-known that long-range corrections are very important to correctly describe the behavior of molecular systems with electrostatic interactions. Some properties are, however, much

more sensitive than others to the explicit consideration of those contributions, as, for example, dynamic and dielectric properties[24] as we have referred to in section 2. In order to discuss the role played by electrostatic contributions and to assess the influence of the truncation of long-ranged Coulombic interactions on the vapor—liquid and critical properties of a molecular system, we have carried out Gibbs ensemble simulations with and without the Ewald sum. In addition, we are also reporting the vapor—liquid coexistence curve for a system with the same site—site Lennard-Jones interactions but without charges.

The comparison between the results obtained for those different situations and experimental values is shown in Table 2 and Figure 4. The pressures were only estimated for a few points, and their values were always within 1—6 MPa.

The estimated critical properties and the corresponding experimental values are presented in Table 3.

For the present potential model and number of particles, the vapor—liquid and critical properties do not appear to be significantly sensitive to the Coulombic long-range corrections as can be observed in Table 2 and Figure 4. Nevertheless, the curve obtained without the Ewald sum has a systematic slightly lower order parameter, $\varrho_L - \varrho_V$, than the curve obtained with the Ewald sum. This explains why the corresponding critical temperature is also slightly lower. Both curves are, however, within the standard deviations, and the overall agreement with experiment is good as can also be observed in Table 2 and Figure 4.

The results obtained with the Lennard-Jones model, however, present pronounced deviations relatively to the values obtained with the charged model and to the experimental data. This suggests, clearly, the importance of the dipolar interactions in
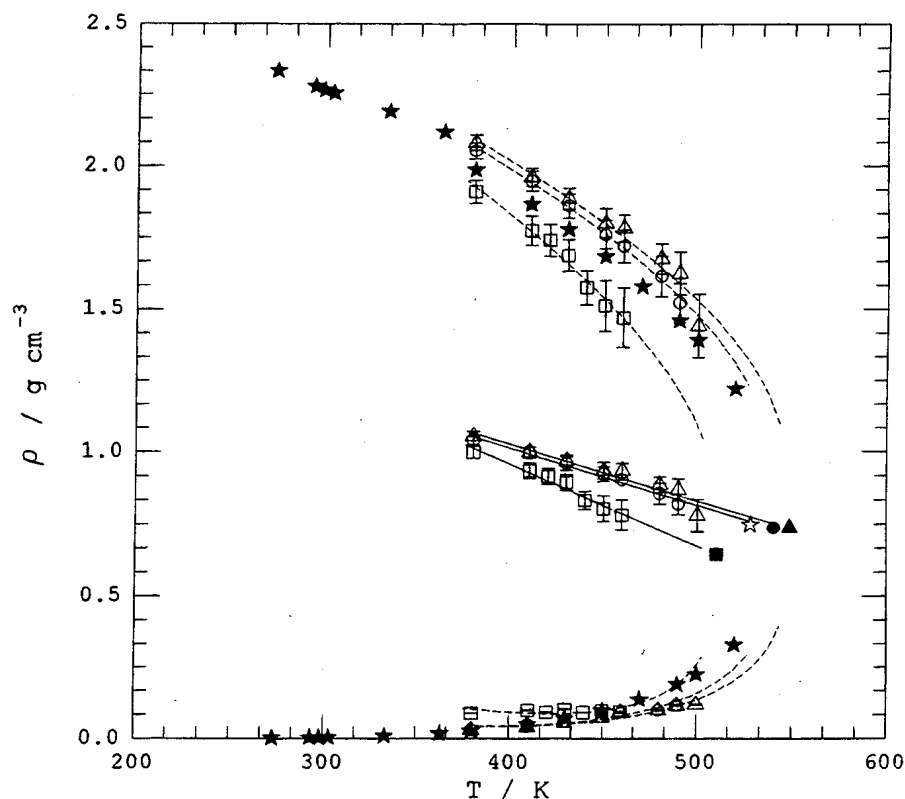
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Figure 4. Vapor—liquid coexistence curves of methyl iodide: (★) experiment, (△) charged model with Ewald sum, (○) charged model without Ewald sum, (□) Lennard-Jones model, (☆) experimental critical point, (▲, ●, ■) estimated critical points, (- - -) fitting, (—) average density.

TABLE 3: Critical Properties of Methyl Iodide

	T_c/K	$\varrho_c/g\ cm^{-3}$
experiment[a]	528	0.747
EW[b]	548.6	0.735
WEW[c]	540.2	0.736
LJ[d]	510.4	0.643

[a] From ref 35. [b] Critical properties with Ewald sum. [c] Critical properties without Ewald sum. [d] Critical properties for the site—site Lennard-Jones system.

methyl iodide. The effect of dipoles on the vapor—liquid coexistence curve of a Stockmayer system has been discussed by Smit et al.[37] and by Van Leeuwen et al.[38] They observed that the critical temperature is an increasing function of the dipole strength but the critical density is not significantly sensitive to it. Our results show a similar behavior as far as the critical temperature is concerned. The addition of a charge distribution to the Lennard-Jones system increases the critical temperature as well the critical density as can be observed in Table 3. The addition of charges increases the cohesiveness of the system, which is reflected by a higher order parameter and explains the higher critical temperature of the charged model.

We should mention that we were not able to find experimental results on the vapor—liquid equilibrium of methyl iodide in the temperature range probed in the present GE simulations although an extensive search in the literature has been done. Therefore, we have estimated some experimental results for that range from experimental results at other temperatures. Thus, in Figure 4, the first six results of the liquid branch at lower temperatures are real experimental results.[34,39] The other points were estimated by fitting those six experimental values and the experimental critical properties to the law of rectilinear diameters. The experimental densities of the vapor were estimated by fitting experimental vapor pressures[40] to the Clausius—

Clapeyron equation and using them in the van der Waals equation of state. The soundness of the procedure was firstly tested with experimental vapor—liquid results for methyl chloride.[41]

4. Concluding Remarks

NPT and Gibbs ensemble Monte Carlo simulations for a site—site model of methyl iodide have provided much information about the liquid, vapor—liquid, and critical properties of the system. The structure of liquid methyl iodide reflects energetic competition between dimers and illustrates the role played by dipolar Coulombic contributions in the liquid phase where a significant number of antiparallel dimers are present. Those dipolar contributions are also shown to be very important for the vapor—liquid and critical properties of methyl iodide. For the present potential model and number of particles, our results suggest that the vapor—liquid and critical properties are not significantly sensitive to the Coulombic long-range corrections.

The overall agreement of our simulated results with experimental data is rather good, suggesting that our potential model is sufficiently accurate to reproduce a wide range of experimental properties of methyl iodide. To our knowledge, the present study is also one of the first computer simulations of the phase coexistence for a realistic model of a dipolar system.

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