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Abstract. Monte Carlo simulations of the liquid–vapour interface for a site–site intermolecular potential of methylchloride are reported. The introduction of non-uniform samplings for computer modelling of non-uniform systems has been considered and it is suggested that they may be of interest when the transition region is an important portion of the whole system. The role played by dipolar coulombic interactions in the interfacial properties has been discussed and the results of the simulations for a system without charges (LJ system) are reported. The interfacial transition region has been studied from both the structural and the energetical point of view. The orientational order in the transition region reflects the competition between anisotropy of the site–site potential and the orientational ordering induced by dipolar interactions. The surface tensions (γs) are not significantly dependent on the size of the system but are very sensitive to the long-range corrections. Our best estimate for γ at 200 K is 36.6 ± 2.4 erg cm^{-2} which is not in very good agreement with the experimental value (26.5 erg cm^{-2}). The coulombic contribution to the surface tension accounts for 25% of the total value (7.7 erg cm^{-2}). It is suggested that the differences between the results from simulations and experiments for γ may be related to the inadequacy of effective pairwise additive intermolecular potentials parametrized to reproduce bulk properties to model the behaviour of non-uniform systems.

1. Introduction

Computer simulation techniques (Monte Carlo MC and molecular dynamics) have been extensively used to study the structural and thermodynamical properties of uniform condensed phases (Allen and Tildesley 1987). For homogeneous systems, the dependence of the results on the number of particles and on the sum convention is relatively well known and methods to take into account long-range coulombic interactions, as lattice summations (Ewald's sum) and reaction field techniques, are now standard procedures. However, studies of non-uniform systems by computer simulation are relatively less frequent. This can be related to the fact that the simulation of non-uniform systems may require a systematic analysis of the size

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dependence and of the sum convention. This analysis is very important to make the results accurate and to validate any comparison of computer simulations with theoretical and experimental information.

Several applications of computer simulation methods to the study of interfacial properties and in particular the liquid–vapour interface have been reported. Thus, some works reported computer simulations of the liquid–vapour interface of Lennard–Jones (LJ) systems (Liu 1974, Rao and Levesque 1976, Miyazaki *et al* 1976, Chapela *et al* 1977, Nijmeijer *et al* 1988). Extensions to Stockmayer liquids (Eggebrecht *et al* 1987b), homonuclear diatomics without quadrupolar interactions (Thompson and Gubbins 1978, 1979) and with quadrupolar interactions (Thompson and Gubbins 1981, Gubbins 1986) have been also reported. The influence of long-range electrostatic interactions on interfacial properties of a quasi-Stockmayer system has been recently discussed (Hertzner *et al* 1991). MC (Lee and Scott 1980, Borštnik *et al* 1980) and molecular dynamics (Matsumoto and Kataoka 1988, Wilson *et al* 1988, Motakabbir and Berkovitz 1991, Towsend and Rice 1991) simulations of the vapour liquid interface of water and methanol (Matsumoto and Kataoka 1989) have been carried out. The most recent applications reflect the great interest in studying interfacial properties of molecular systems by computer simulation, using realistic intermolecular models. Other theoretical studies on the interfacial properties of dipolar systems based the solution of integral equations (Eggebrecht *et al* 1987a) and on density functional theory (Teixeira and Telo da Gama 1991) have also been reported. An extended mean-field density functional theory has been applied to discuss the orientational structure of the water liquid–vapour interface (Yang *et al* 1991).

The main objectives of computer simulations of non-uniform molecular systems are to calculate the density and orientational profiles and the value of the surface tension. However, previous studies (Chapela *et al* 1977, Nijmeijer *et al* 1988) pointed out some relevant features in the simulation of non-uniform systems which merit some special attention. One important aspect is related to the dependence of the results, in particular of the surface tension and interfacial thickness, on the number of particles and on the sum convention. Another aspect concerns the use of effective potentials parametrized to study uniform condensed phases (Jorgensen 1986), to model the behaviour of non-uniform systems. These facts suggest that modelling of interfacial properties by computer simulation needs some complementary analysis in order to clarify the meaning of their results.

We are reporting in this work an MC simulation of the liquid–vapour interface for a site–site intermolecular model (TIPSE) of methylchloride (Bigot *et al* 1985, Cabral *et al* 1987). We present results for the density and orientational profiles and for excess surface properties at 220 K. The relative importance of coulombic (dipolar) interactions on the interfacial properties has been discussed performing simulations for a model without charges. A detailed analysis of the dependence of the results on the number of particles and on the cut-off radius has been carried out. We have also discussed the introduction of non-uniform sampling to study interfacial properties.

2. Theoretical overview

When we study a molecular, non-uniform fluid, the quantities of greatest interest are the one-particle distribution function and the surface tension. For diatomic (or more generally, two sites of interaction) molecules, the orientational variable of interest is

the angle θ between the molecular axis and the z axis. For this reason, we can use the following expansion for the density–orientation profile (Thompson and Gubbins 1978)

$$\rho(z,\theta) = \sum_{k=0}^{\infty} \rho_k(z) P_k(\cos\theta) \tag{1}$$

where $P_k(\cos\theta)$ is a Legendre polynomial. This function can be related to the density profile through the equation

$$\rho(z) = \int_0^{\pi} \rho(z,\theta) \sin\theta\, d\theta. \tag{2}$$

The individual coefficients $\rho_k(z)$ of the expansion (1) are given by (Abramovitz and Stegun 1965)

$$\rho_k(z) = \frac{2k+1}{2} \int_0^{\pi} \rho(z,\theta) P_k(\cos\theta) \sin\theta\, d\theta. \tag{3}$$

For computational purposes $\rho_k(z)$ can be written as

$$\rho_k(z) = \{[(2k+1)/2]/S_{xy}\delta z\}\langle\langle P_k(\cos\theta)\rangle\rangle \tag{4}$$

where S_{xy} is the surface area and δz is the thickness of a slab along the z axis. The symbol $\langle\langle\ \rangle\rangle$ means a configurational average over every molecule with centre of mass in a slab over z with thickness δz.

For the calculation of the surface tension we used a relation proposed by Thompson and Gubbins (1978)

$$\gamma = \frac{1}{S_{xy}} \left\langle \sum_{i<j} \frac{x_{ij}^2 - z_{ij}^2}{r_{ij}} \sum_k \frac{r_k \cdot r_{ij}}{r_k r_{ij}} u'(r_k) \right\rangle \tag{5}$$

where $\langle\rangle$ means a configurational average and $u'(r_k)$ means the derivative of the potential with relation to r_k. We observed that i and j refer to the molecular centre of mass and k to the different interaction sites.

In order to discuss the structure of the interface and to calculate some quantities usually defined to characterize it, we have fitted the density, the average energy per particle and the energetical volumic density profiles to some functionals. In this sense, there have been, over the years, several theoretical attempts to find a functional form to fit interfacial profiles. Cahn and Hilliard (1958) found that the tanh might be a good approximation not only for the density profile but also for any other intensive local parameter (except temperature or pressure). Other fitting functionals were developed by Fick and Widom (1969) and by Buff *et al* (1965). For reasons of simplicity, and since all functional forms give the same results at low temperatures, we have fitted our profiles to tanh functionals, i.e.

$$\rho(z) = \tfrac{1}{2}(\rho_l - \rho_g) - \tfrac{1}{2}(\rho_l + \rho_g)\tanh[2(z - z_{0d})/d_d] \tag{6a}$$

$$u(z) = \tfrac{1}{2}(u_l - u_g) - \tfrac{1}{2}(u_l + u_g)\tanh[2(z - z_{0u})/d_u] \tag{6b}$$

$$u^v(z) = \tfrac{1}{2}(u_l^v - u_g^v) - \tfrac{1}{2}(u_l^v + u_g^v)\tanh[2(z - z_{0v})/d_v] \tag{6c}$$

In expressions (6a–c), $\rho(z)$ denotes the density, $u(z)$ the average energy per particle and $u^v(z)$ the energetical volumic density. Subscripts l and g refer respectively to the liquid and gas phases. The parameter z_0 indicates the location of the Gibbs surface and d is related to the interfacial thickness ($d \simeq 1.10t$) where t is the 90–10 thickness.

3. Computational procedure

3.1. Intermolecular potential

The intermolecular potential for methylchloride (CH_3Cl) used in this study has been reported elsewhere (Bigot *et al* 1985, Cabral *et al* 1987). It is an effective site–site (CH_3 and Cl) intermolecular potential. The dipole moment for this model is $2.13D$ which is higher than the observed gas phase dipole ($1.9D$), taking into account the average polarization of the molecules in condensed phases. This potential correctly reproduces some thermodynamic properties (densities and vaporization enthalpies) for liquid methylchloride (Bigot *et al* 1985, Cabral *et al* 1987). The dimerization energy for this model is -2.1 kcal mol^{-1} for anti-parallel molecules at a distance of 3.9 Å between the geometrical centres. Suppression of the charges (defining a site–site LJ system) leads to a dimerization energy of -1.2 kcal mol^{-1} for the same distance. However, for the LJ system the most stable dimer is parallel which illustrates that for the TIPSE model orientational order is determined by competition between site-site LJ and dipolar contributions (Lomba *et al* 1991).

3.2. Simulation details

For the initial configurations, we have placed a given number of molecules (128, 512 or 1024) in a cubic box with a side appropriate to reproduce the experimental (Gallant 1968) number density of liquid CH_3Cl (0.0124 Å^{-3}) at 220 K (21.771 Å, 34.526 Å and 43.500 Å, respectively). The configurations were generated using the Metropolis MC (Metropolis *et al* 1953) algorithm. Periodic boundary conditions were applied in all directions. The potential energy and the surface tension have been calculated taking into consideration the interaction of one central molecule with the set of molecules and nearest periodic images inside a sphere of radius R_c (the cut-off distance).

After a period of equilibration (2.0×10^6 configurations) we increased the dimension of the box along the z axis. Another period of $\sim 2.0 \times 10^6$ configurations was needed to enable the stabilization of the interface. For the production phase several runs, in groups of ten, each of 10^5 configurations, have been carried out. For each run we calculated the potential energy of the system, the surface tension, the density profile, the first and second coefficients of the Legendre expansion, and the profiles of average energy per molecule for each one of the contributions (R^{-12}, R^{-6} and R^{-1}). Using the set of ten values we calculated the sub-averages and the corresponding error for each quantity (we accepted the standard deviation as a good estimate for the error). These sub-averages and errors were used to calculate the final averages and errors. For the fittings we used a least-squares method. Since this is a non-linear problem there was no simple way to estimate the errors of our parameters, and for this reason we divided the results in larger groups of five averaged profiles and calculated the average and standard deviation of those adjustments.

For some systems we have also studied the possibility of introducing a non-uniform sampling procedure. The motivation behind this initiative lies in the fact that the calculation of the surface tension depends mainly on the contributions from the molecules in the transition region (Nijmeijer *et al* 1988). Different functions for the non-uniform sampling were used. In all of them, the probability for a particular molecule to be sampled was dependent on its z coordinate of the centre of mass. We observe that non-uniform samplings are widely used in MC simulations of dilute

solutions (Owicki 1978) and its efficiency supports the adequacy of the introduction of 'unphysical' procedures by MC methods in order to improve the sampling of the configurational space.

The runs have been carried out on Convex computers (C220 and C3410). On the last machine a run with 10^5 configurations for a system with 512 molecules and a cut-off distance of 12.5 Å took almost 15 min.

4. Results and discussion

4.1. Density profiles

The density profiles for the simulations with 128, 512 and 1024 particles using different values of R_c are presented in figures 1 and 2. We have verified that our profiles could be very well fitted by a tanh functional, reflecting, in contrast to the results reported by Matsumoto and Kataoka (1988) for water, that no specific interfacial structure occurs for our model of methylchloride. Figure 1 shows the results for different sampling procedures (uniform, linear and non-uniform) for 128 molecules. The simulation of the liquid–vapour interface for the TIPSE model of methylchloride at 220 K using a small number of particles (128) may lead to the appearance of a meta-stable structure (figure 1). The introduction of a non-uniform sampling proportional to z^4 ($z4$) stabilizes the interface while the use of a linear sampling (proportional to z), although stabilizing the system, leads to an artificial structure in the bulk region close to the interface (figure 1). The appearance of meta-stable structures in the simulation of non-uniform systems seems to be associated with situations in which the transition region represents an important portion of the whole system (Matsumoto and Kataoka 1989). It seems that in these cases the use of non-uniform sampling could be of interest.

Figure 2 illustrates that the density profiles are not significantly sensitive to the number of particles or to the value of R_c. We report in table 1 the density profile parameters fitted to a tanh functional. We observe that the fitted bulk densities are the same as that from a simulation of the uniform system performed with 1024 molecules and $R_c = 10.5$ Å (0.01242 ± 2 Å^{-3}), a result in very good agreement with the experimental data for the bulk density (Gallant 1968). We have detected a small increase of the interfacial thickness when we move from the system of 128 molecules (3.42 ± 64 Å) to that with 1024 molecules (4.15 ± 15 Å). The dependence of the interfacial thickness on the surface area has been discussed by Chapela *et al* (1977) for LJ systems and by Thompson and Gubbins (1981) for site–site LJ, and site–site LJ plus a (quadrupolar) charge distribution. This effect is related to the damping of all surface waves of wavelength greater than the width of the simulation box (Chapela *et al* 1977). In the present study there is a change of 20% in the interfacial thickness with an enlargement of S_{xy} by a factor of 3.99, a result which is in agreement with those of Chapela *et al* (1977) but is lower than the value of Thompson and Gubbins (1981) which reported a change of 23% in the interfacial thickness with an enlargement by a factor of 2.43 of S_{xy}. However, as is illustrated in table 1, the interfacial thickness involves large error bars and it seems that there is no evidence of dependence of the interface growth with S_{xy} on the specific nature of intermolecular interactions.

Another interesting result is the enlargement of the interfacial thickness ($\sim 25\%$) as a consequence of the suppression of the dipolar moment of methylchloride, reflecting that the coulombic dipolar interactions contribute to reducing the size
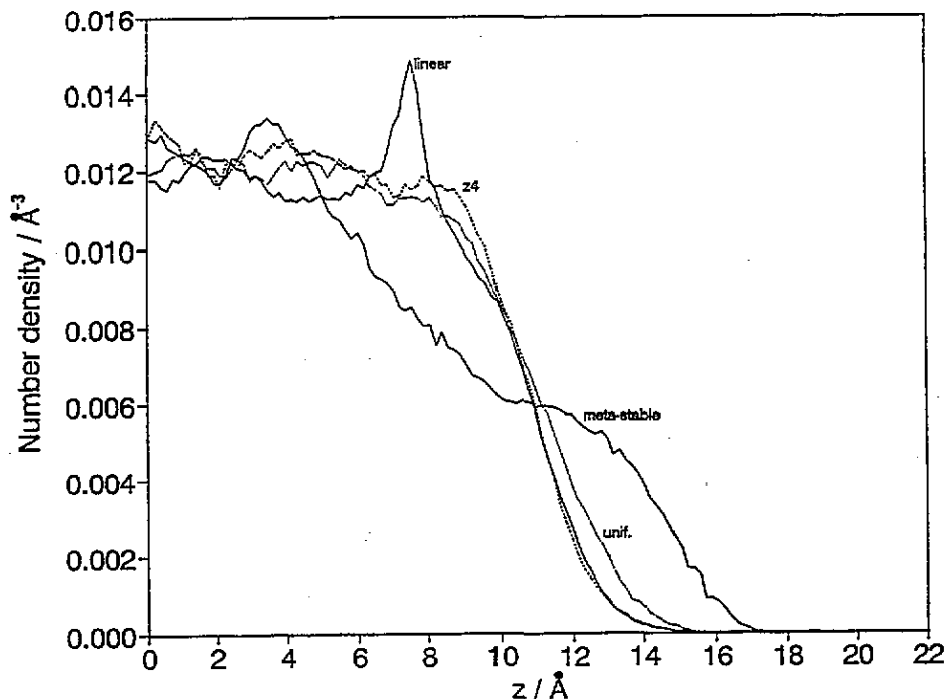
Figure 1. Density profiles for the system with 128 molecules using different samplings. The presence of a meta-stable state is illustrated.

of the transition region and to increasing the value of the surface tension. The dependence of the interfacial thickness and surface tension on the adding of coulombic (quadrupolar) contributions has been discussed by Thompson and Gubbins (1981). They verified that for a diatomic site–site model of N_2 and Cl_2, some sensitivity of the results to the presence of quadrupolar interactions could be detected and that they contributed to a steepening of the density profile and to increasing the surface tension.

A recent density functional study on the influence of dipolar interactions on interfacial structure and surface tension has been reported (Teixeira and Telo da Gama 1991). The addition of a dipole moment increased the surface tension, and interfacial ordering induced by purely dipolar forces has been detected. Our results are in agreement with these predictions; however we emphasize that in our study, interfacial ordering and excess properties are determined by two coupled and competing effects, namely, site–site anisotropy and coulombic interactions (Lomba *et al* 1991).

4.2. Orientational profiles

The orientational profiles are presented in figures 3 and 4. We can observe (figure 3) that $\rho_1(z)$ fluctuates around zero suggesting that none of the sites has a tendency to be orientated to the vapour phase (on the liquid side) or *vice versa*. Thus, it seems that for methylchloride there is no preferential orientational order of the dipoles close to the interface. In contrast with this result, if we make the charges equal to zero some sort of orientational order can be detected (figure 3(b)). More precisely, we can
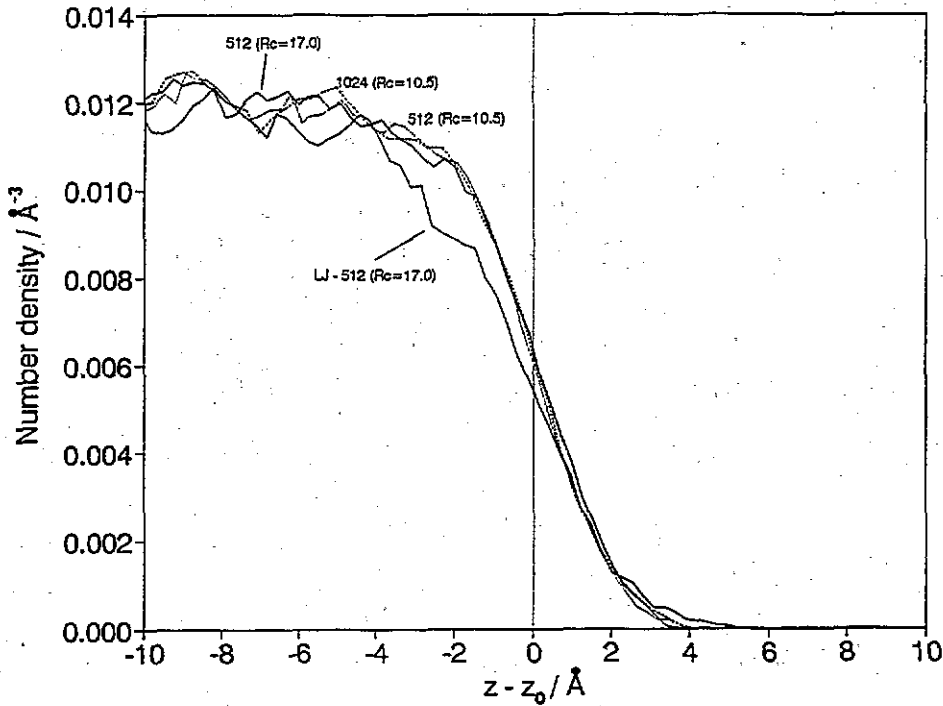
Figure 2. Density profiles for the systems with 512 and 1024 molecules using different values of R_c (cut-off radius). LJ-512 represents the density profile for a system with the charges equal to zero.

Table 1. Density profile interfacial parameters.

N	R_c (Å)	Sampling	Conf. ($\times 10^7$)	z_{0d} (Å)	d_d (Å)	ρ_l (Å^{-3})	ρ_g (Å^{-3})
128	10.5	uniform	3.0	11.10 ± 5	4.63 ± 57	0.01206 ± 3	0
128	10.5	linear	5.0	10.74 ± 4	3.73 ± 35	0.01245 ± 8	0
128	10.5	z4	3.0	10.85 ± 3	3.42 ± 64	0.01232 ± 8	0
512	10.5	uniform	2.9	17.70 ± 5	3.93 ± 10	0.01204 ± 6	0
512	12.5	uniform	3.0	17.56 ± 12	4.05 ± 42	0.01214 ± 6	0
512	17.0	uniform	3.0	17.49 ± 4	4.45 ± 49	0.01224 ± 4	0
512	10.5	z4	2.2	17.11 ± 8	4.41 ± 33	0.01249 ± 6	0
1024	10.5	uniform	3.0	22.19 ± 5	4.15 ± 15	0.01214 ± 3	0
LJ-512	10.5	uniform	3.0	18.33 ± 12	5.08 ± 57	0.01166 ± 7	0
LJ-512	17.0	uniform	2.3	18.03 ± 7	5.57 ± 62	0.01182 ± 6	0

see that the methyl site has a tendency to orientate towards the liquid in the region of the interface after the Gibbs surface (on the vapour side). This result reflects the fact that for heteronuclear diatomics some sort of orientational order along the interface can be observed. The explanation of the behaviour of methylchloride is probably related to the competition between the opposite orientational tendencies induced by site–site LJ and dipolar interactions.

The $\rho_2(z)$ coefficient is presented in figure 4. A well defined orientational structure for the transition region can be observed. The behaviour of $\rho_2(z)$ (figure 4(a)) allows us to conclude that the molecules orientate preferentially perpendicular
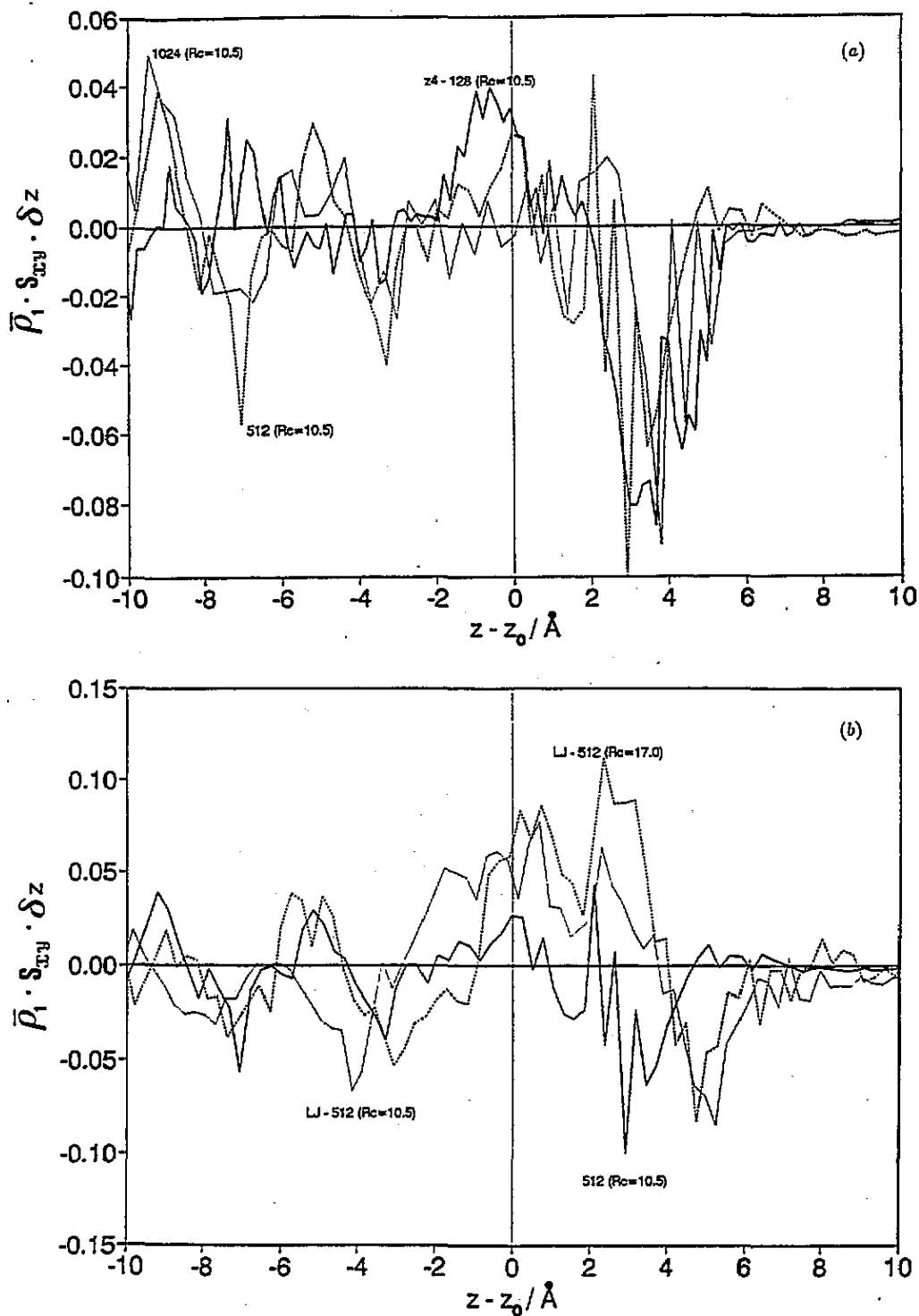
Figure 3. Orientational density profiles $\rho_1(z)$: (*a*) orientational profile $\rho_1(z)$ for methylchloride using different numbers of molecules and R_c values; (*b*) comparison between $\rho_1(z)$ for methylchloride and for the LJ system.

Figure 4. Orientational density profiles $\rho_2(z)$: (*a*) orientational profile $\rho_2(z)$ for methylchloride using different numbers of molecules and R_c values; (*b*) comparison between $\rho_2(z)$ for methylchloride and for the LJ system.
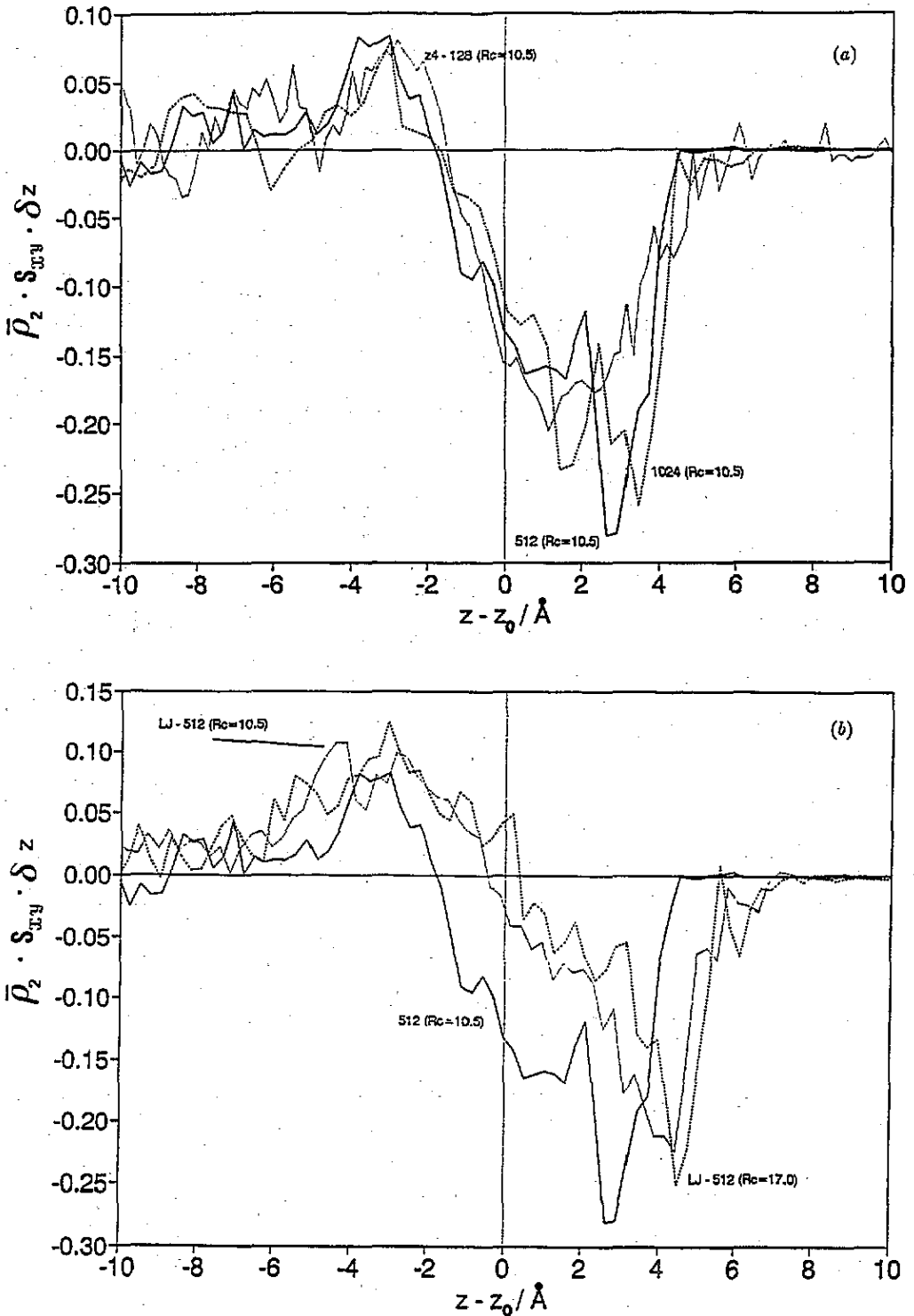
to the Gibbs surface (S) on the liquid side and parallel to this surface on the vapour side. This structure is similar to that observed for diatomic LJ molecules (Thompson and Gubbins 1978, Thompson and Gubbins 1981). Comparison between $\rho_2(z)$ for methylchloride and the LJ system (figure 4(b)) shows that the suppression of the charges contribute to orientating the molecules perpendicular to the interface (increasing the number of molecules perpendicular to S on the liquid side and reducing the number of molecules parallel to S on the vapour side). The orientational order induced by the dipoles in the present study is in agreement with the results for the Stockmayer fluid (Eggebrecht *et al* 1987a, b, Teixeira and Telo da Gama 1991). However, in contrast with the simulation results for the Stockmayer system which indicates that the dipolar interactions tend to orientate the molecules parallel to the Gibbs surface along all the transition region, our results indicate a preferential tendency for the molecules to orientate perpendicular to the surface on the liquid side. Comparison between several studies on the orientational order along the liquid–vapour interfaces for different systems suggests that the observed inversions of this order on the liquid side and on the gas side could be related to the competition between energetical and entropic factors (Teixeira and Telo da Gama 1991).
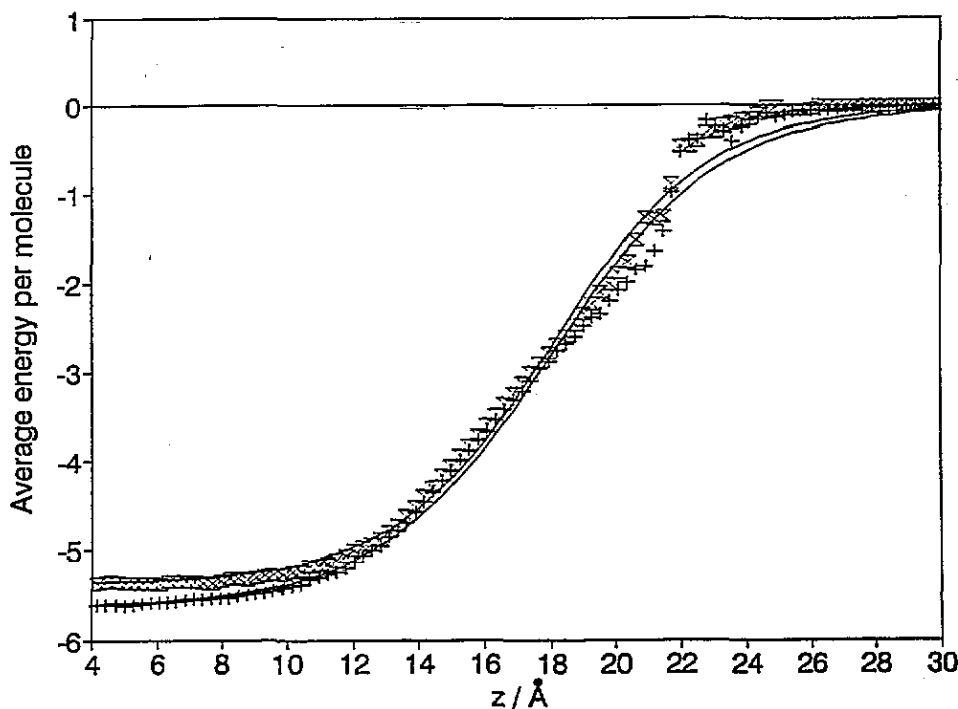

Figure 5. Average energy per molecule profiles for methylchloride (512 molecules): ⅄, $R_c = 10$ Å; +, $R_c = 17$ Å. Full curves are tanh least-squares fitted functions to simulation profiles.

4.3. Energy profiles

In order to complement the information provided by the analysis of the density profile we are reporting the average energy per particle profile and the volumic density
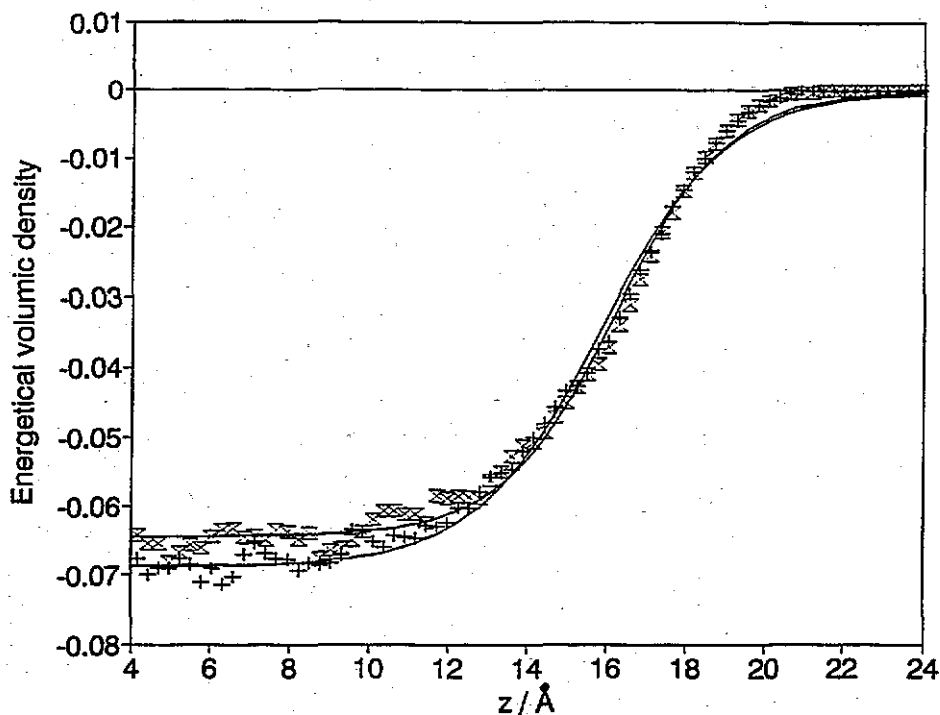
Figure 6. Energetical volumic density profiles for methylchloride (512 molecules): ⟨, R_c = 10 Å; +, R_c = 17 Å. Full curves are tanh least-squares fitted functions to simulations profiles.

of energy profile. These profiles and the corresponding fitted functions given by expressions (6a) and (6b) are presented in figures 5 and 6. The set of fitted parameters characterizing the energetical interface (z_{0u}, d_u, u_l etc) are reported in tables 2 and 3. For both profiles our results suggest a small increase of the energetical interfacial thickness with the number of molecules. The results also indicate a decrease in the adjustment errors with the growth of the system. The reason for this might be the larger portion of the system in the bulk phase, which improves the fitting of the bulk densities. The fitted energetical volumic densities for the liquid (u_l^v) are in very good agreement with the results from the simulation of the bulk phase with 1024 particles and R_c = 10.5 Å (u_l^v = −0.0676±2 kcal mol^{-1} Å^{-3}). Comparison between the results for the LJ system (charges equal to zero) and methylchloride shows, in agreement with the conclusions for the density profile, an increase in the energetical interfacial thickness.

Table 2. Average energy per particle profile interfacial parameters.

N	R_c (Å)	Sampling	z_{0u} (Å)	d_u (Å)	u_l (kcal mol^{-1})
512	10.5	uniform	18.05 ± 5	9.58 ± 52	−5.38 ± 3
512	17.0	uniform	18.01 ± 18	10.55 ± 60	−5.63 ± 2
1024	10.5	uniform	22.71 ± 12	10.22 ± 37	−5.41 ± 2
LJ-512	10.5	uniform	18.80 ± 30	10.98 ± 71	−4.36 ± 3
LJ-512	17.0	uniform	18.68 ± 33	11.44 ± 70	−4.62 ± 2

Table 3. Energetical volumic density profile interfacial parameters.

N	R_c (Å)	Sampling	z_{0v} (Å)	d_v (Å)	u_1^v (kcal mol^{-1} Å^{-3})
512	10.5	uniform	16.23 ± 6	5.74 ± 10	-0.0645 ± 4
512	17.0	uniform	15.87 ± 4	6.39 ± 36	-0.0688 ± 2
1024	10.5	uniform	20.66 ± 6	6.06 ± 14	-0.0655 ± 4
LJ-512	10.5	uniform	16.67 ± 10	6.43 ± 57	-0.0504 ± 5
LJ-512	17.0	uniform	16.28 ± 12	6.90 ± 50	-0.0542 ± 4

We have also studied the interfacial behaviour of the different energetic contributions (R^{-12}, R^{-6} and R^{-1}) to the intermolecular potential. Using a similar fitting procedure we have determined the position of the Gibbs surface and the values of the interfacial thickness for each of these contributions (table 4). Our results suggest that the 'coulombic bulk region' is significantly more important than the bulk region to the other contributions. This conclusion is based on the positions of the Gibbs surface z_{0u} for each one of the contributions. It can be also observed that the interfacial thickness is slightly reduced for the coulombic contribution compared to R^{-12} and R^{-6}. These results indicates that the coulombic dipolar interactions play a particular role in the definition of the transition region, contributing to reducing the dimension of the structural and energetical transition regions. In addition, comparison between the relative contribution of the coulombic energy to the total energy of the bulk (17%) and to the surface tension (see section 4.4), which is 25%, reinforce the conclusion on the important role played by dipolar interactions in the transition region.

Table 4. Different contributions to the average energy per particle.

N	R_c (Å)	Contribution	z_{0u} (Å)	d_u (Å)	u_1 (kcal mol^{-1})
512	10.5	coulombic	18.99 ± 6	8.89 ± 52	-0.928 ± 4
		attractive	17.42 ± 6	9.37 ± 46	-8.60 ± 6
		repulsive	16.98 ± 8	8.89 ± 42	4.14 ± 4
512	17.0	coulombic	19.23 ± 31	9.34 ± 78	-0.904 ± 7
		attractive	17.27 ± 15	10.24 ± 63	-9.03 ± 3
		repulsive	16.76 ± 13	9.70 ± 69	4.30 ± 2
1024	10.5	coulombic	23.72 ± 13	9.44 ± 48	-0.933 ± 3
		attractive	22.03 ± 11	9.99 ± 39	-8.65 ± 5
		repulsive	21.56 ± 12	9.53 ± 38	4.17 ± 4

The most important aspect when we compare structural and energetical profiles is the significant difference between the interfacial thickness in energetical terms (d_u, d_v) and in structural (d_d) terms. We can see that the interfacial thickness (d_u) related to the average energy per particle profile is a factor of ~ 2.4 larger than for the density profile and that d_v is ~ 1.5 larger than d_d illustrating that the transition region is much wider from the energetical point of view. It is not clear what criteria should be preferred to characterize the transition region although until recently theoretical studies have been directed toward the analysis of the structural density profile.

4.4. Excess surface properties

Table 5 reports the excess surface properties for the liquid–vapour interface of methylchloride. The data include the surface tension γ (the surface excess Helmholtz

free energy) and u_s (the surface excess internal energy) which can be obtained assuming tanh-type profiles as (Matsumoto and Kataoka 1989)

$$u_s = (u_l^v - u_g^v)(z_{0d} - z_{0v}).\qquad(7)$$

The surface excess entropy s_s has been also calculated through the expression

$$\gamma = u_s - Ts_s.\qquad(8)$$

For the surface tension γ our results suggest a small dependence on the number of particles. This effect could be related to the decrease in the interfacial thickness previously analysed, and it is coherent with theoretical predictions of the interfacial thickness dependence on the surface area. Another important point concerns the dependence of the surface tension on the cut-off radius (R_c). Our results show that this quantity is sensitive to R_c but that the differences between γ for 512 molecules with $R_c = 15$ Å (36.9 ± 2.5 erg cm^{-2}) and $R_c = 17$ Å (36.6 ± 2.4 erg cm^{-2}) suggest that a limit value has been attained. Comparison between the theoretical values of table 5 with the experimental surface tension of CH$_3$Cl at 220 K, which is 26.5 erg cm^{-2} (Gallant 1968) shows that the agreement is not good. However, we should observe that the quality of the agreement is sensitive to the number of molecules and to the cut-off radius. The coulombic contribution to the surface tension has been calculated for a system of 512 molecules and $R_c = 10.5$ Å. It is 7.7 ± 3.6 erg cm^{-2}, which corresponds to 25% of the total value (31.1 ± 2.7 erg cm^{-2}).

Table 5. Excess surface properties.

N	R_c (Å)	Sampling	Conf. ($\times 10^7$)	γ (erg cm^{-2})[a]	u_s (erg cm^{-2})	s_s (erg cm^{-2} K^{-1})	$sA(R)$
512	10.5	uniform	2.9	31.1 ± 2.7	65.9 ± 3.5	0.158 ± 20	2.40 ± 31
512	12.5	uniform	3.0	31.6 ± 2.6			
512	15.0	uniform	1.5	36.9 ± 2.5			
512	17.0	uniform	3.0	36.6 ± 2.4	77.5 ± 2.7	0.186 ± 17	2.79 ± 25
512	10.5	z4	2.2	29.6 ± 2.5			
1024	10.5	uniform	3.0	29.7 ± 3.1	69.6 ± 3.6	0.181 ± 22	2.74 ± 33
LJ-512	10.5	uniform	3.0	21.5 ± 2.4	58.1 ± 4.3	0.166 ± 27	2.51 ± 41
LJ-512	15.0	uniform	1.2	28.3 ± 2.4			
LJ-512	17.0	uniform	2.3	31.1 ± 2.1	65.9 ± 5.3	0.158 ± 26	2.38 ± 39

[a] Experimental value: 26.5 ± 1 (Gallant 1968).

In order to assess the importance of the coulombic dipolar contributions to the interfacial properties we have also reported in table 5 the surface excess properties for the LJ system. The results show a reduction of the surface tension for the LJ system which is coherent with the previous result for the contribution of the coulombic interactions. However, the most significant result concerns the dependence of γ on the cut-off radius for the two systems, methylchloride and the LJ system. We could expect that long-range interactions would be more important to correct the evaluation of the surface tension for methylchloride than for the corresponding LJ system. However, this seems to be not the case for our system at the present thermodynamic conditions. In fact, an increase of R_c by 2.0 Å (from 15 Å to 17 Å) leads to almost the same value of γ for methylchloride while the same variation of R_c increases γ by 10% for the system with the charges equal to zero. A possible

explanation for this apparently anomalous results can be found in the dimensions of
the transition region for both systems. We have illustrated in the previous section
that the transition energy for the LJ system is wider than that for methylchloride.
This is true from the structural and also from the energetical point of view. If
we assume that molecules which are in the transition region are those that most
significantly contribute to the surface tension, it seems reasonable to assume that the
cut-off radius should be chosen in order to include for one molecule in this region, at
least, all the others in the transition region. In addition, it should be certainly more
adequate to define the transition region in energetical terms.

   We can also observe an increase in the excess internal energy and the surface
excess entropy with the cut-off radius. This fact is coherent with the behaviour of the
surface tension, since these quantities are predominantly related to the dimension of
the transition region. The small reduction in the excess entropy for the LJ system is
probably not significant within the error bars.

   We have also calculated the molar surface entropy (sA) defined as (Good 1957)

$$sA = 1.10\rho_1^{-2/3} N_A s_s \qquad (9)$$

where N_A is the Avogadro number. From the results of table 5, using the criterion
discussed by Good (1957), the calculated molar surface entropy is in the range
of values $2.0R$–$2.7R$ which is coherent with the fact that methylchloride may be
classified as a polar fluid without hydrogen bonds.

5. Conclusions

Monte Carlo simulations of the interfacial properties for a site–site model of
methylchloride provided us with some important data to discuss the structure of
the liquid–vapour transition region of a molecular dipolar system. The most
important conclusion concerns the role played by the different contributions to the
intermolecular potential, to the density and orientational profiles, and to the excess
properties of methylchloride. It is suggested that for a realistic site–site model
of methylchloride, the interfacial structure depends on the competition between
Lennard–Jones and coulombic interactions. Another relevant aspect is related to
the definition of the transition region in structural and energetical terms, which is
quite different for this system and for the present thermodynamic state. In this sense,
it appears that the correct criterion for the adequate definition of the cut-off radius,
to correct long-tail contributions to the surface tension, should be made from the
analysis of the size of the transition region and not necessarily from the nature of the
long-range behaviour of the intermolecular potential. This conclusion is supported by
the well known fact about the difficulty of correctly evaluating in computer simulations
the surface tension closer to the critical point where the dimension of the transition
region is significantly increased. The reason is certainly related to the importance of
including in the calculation all the molecules in this region.

   Another conclusion concerns the differences between our theoretical evaluations
for the surface tension of methylchloride and the experimental value. We should
observe that previous simulations of water (Matsumoto and Kataoka 1988) and
methanol (Matsumoto and Kataoka 1989) using realistic intermolecular potentials
indicated some significant differences between calculated and experimental surface

tensions. Thus, for water the surface tension was only half of the experimental value and for methanol differences of 20% have been observed. However, it is difficult to assess the meaning of these results since no analysis has been reported of the dependence on the size and on the long-range corrections. It seems reasonable to assume that these differences would be related to the fact that the intermolecular models used in their simulations were proposed to correctly reproduce the properties of the bulk liquid phase, and it is not clear if they are adequate to model the behaviour of non-uniform systems.

A possible alternative to model the behaviour of non-uniform systems would be the utilization of intermolecular potentials, including the many-body induction interactions (Cabral *et al* 1987). In this sense, a recent study on the water liquid–vapour interface, by Motakabbir and Berkovitz (1991) compared the utilization of polarizable and non-polarizable intermolecular potentials. They pointed out a sensitive dependence of the total average dipole moment per molecule on the local density along the interface, but they have not detected any significant change on the density and orientational profiles in comparison with the pairwise additive model. Unfortunately, these authors have not reported values for excess surface properties and it is expected that these properties should be very sensitive to the local value of the dipole moment and to the orientational correlations induced by them.

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