Surface Tension of the Restrictive Primitive Model for Ionic Liquids

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Hybrid molecular dynamics and Monte Carlo simulations are performed to study the liquid-vapor interface of the restricted primitive model (RPM) of ionic fluids. We report for the first time simulation results of the surface tension associated to this interface. The RPM accurately predicts experimental surface tensions of ionic salts and good agreement with theoretical predictions that include the idea of ion association is found. The simulation results indicate that the structure of an ionic liquid-vapor interface is rather rough. This is reflected in the interfacial thickness, larger than that observed in simple fluids and water.

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Molten salts, electrolyte solutions, and charged colloidal suspensions are examples of systems in which the dominant interparticle forces are the electrostatic interactions. The restricted primitive model (RPM) is the simplest model to study these systems. Despite its simplicity it reproduces many of the important phenomenology observed in ionic systems, in the case of some properties even at a quantitative level [1,2].

Early simulations by Vel'yaminov and Chasovskikh [3] and theoretical studies by Stell, Wu, and Larsen [4] gave the first insights on the now established existence of a liquid-vapor transition in the RPM. Since then, computer simulations have played an important role in providing a quantitative description of the liquid-vapor coexistence curve [5–7] as well as its criticality class [8–10]. Simulation results of the RPM have shown that the vapor phase consists of strongly associated neutral clusters [11,12]. More recent works have considered also the solid-fluid equilibrium [13,14]. Despite all these works, to our knowledge there are no previous simulation studies of the interfacial properties of the RPM. Some studies of ionic liquid-vapor interfaces have considered realistic potentials of molten salts at temperatures close to triple point conditions [15–17], but there are no previous studies at temperatures closer to the critical point temperature. Theoretical predictions based on density functional and integral equations theories indicate that the interfacial properties of an ionic system might depart significantly from the behavior observed in simple fluids [18–20]. Generally speaking, the analysis of the interfacial properties of ionic liquids is important, not only from a fundamental point of view, but also due to their potential technological applications as solvents with environmental uses [21].

In this work we consider the computer simulation of the liquid-vapor interface of the RPM and we provide, for the first time, simulation results of the surface tension of the liquid-vapor interface.

The RPM consists of N charged hard spheres of equal diameter σ embedded in a structureless background with dielectric constant ϵ_m. Global electroneutrality is assumed in such manner that $N/2$ spheres carry positive charge and the rest negative. The interaction potential between two particles, separated by a distance $r = |\mathbf{r}_i - \mathbf{r}_j|$, is given by

$$u(r) = \begin{cases} +\infty, & r < \sigma, \\ \frac{e^2}{4\pi\epsilon_o}\frac{Z_i Z_j}{r}, & r \geq \sigma, \end{cases} \tag{1}$$

where $\mathbf{r}_i$ and Z_i are the position and the valence of ion i, respectively, e is the electronic charge, and ϵ_o is the vacuum dielectric permittivity. The ions are contained in a volume V, with reduced density $\rho^* = N\sigma^3/V$ and reduced temperature $T^* = k_B T/\varepsilon$, where $\varepsilon = e^2/4\pi\epsilon_o\sigma$, k_B is the Boltzmann's constant, and T is the absolute temperature. Hereafter we assume $\epsilon_m = 1$.

In order to simulate the RPM we used a hybrid molecular dynamics method (HMD), which combines both the hard sphere (HS) and continuous forces [22]. In addition to the RPM potential, we considered a second model where the HS contribution was replaced by a soft and continuous repulsive interaction, $u^{\text{soft}}(r) = A(\sigma_s/r)^n$. We used this model to assess the order of magnitude of the surface tension of the RPM. In the soft potential case the simulation can be done using conventional molecular dynamics, therefore we can test the validity of the HMD algorithm. The parameters for this soft restricted primitive model (SRPM) were $\sigma_s = 0.95\sigma$, $n = 225$, and $A/\varepsilon = 20\,000$. The velocity Verlet algorithm was used along with the multiple time step technique (MTS) [23] in order to speed up the calculations. The MTS algorithm is needed because the simulation of the liquid-vapor

interface, especially at high temperatures, requires a large number of configurations to accurately obtain the interfacial properties. This fact is connected with the association phenomenon observed in ionic systems, as we will discuss later.

The simulation cell had lengths $L_x = L_y = 7.114\sigma$ and $L_z = 80.0\sigma$ and contained $N = 648$ particles located in a centered liquid slab surrounded by vapor. The electrostatic interactions were handled using the Ewald technique with conducting boundary conditions [24]. The parameters used in the Ewald technique in both RPM and SRPM were $\alpha = 6/L_x$, $k_x^{\max} = k_y^{\max} = 6$, and $k_z^{\max} = (L_z/L_x)k_x^{\max}$. The HMD simulations involved 10^6 times steps of equilibration and additionally 10^7 time steps of production, where one time step represents the movement of N ions.

In addition to HMD simulations, we also performed Monte Carlo (MC) calculations (see Refs. [11,22] for details). These calculations involved larger systems ($N = 1372$) and were restricted to lower temperatures, closer to the triple point. The maximum displacement of 0.06σ gave typical acceptance rates of 40%. The MC simulations involved ten blocks, each consisting of 10^4 steps of equilibration and 10^5 steps of production. The standard deviation of surface tension in HMD and MC simulations was obtained using those blocks.

The simulation of the liquid-vapor interface at high temperatures is far from trivial. Some of the present authors found in a previous work [25] that the ionic liquid close to coexistence has a large tendency to nucleate large cavities. The size of cavities scales with temperature and can reach values of several ion diameters. Due in part to this, at high temperatures very long runs are essential in order to obtain accurate results for the interfacial properties.

The liquid-vapor densities as function of temperature for the RPM and SRPM models are reported in Table I. We find good agreement between our RPM densities and those from Refs. [6,7]. Our results indicate that the SRPM coexistence densities are systematically lower than those of the RPM. The SRPM potential is slightly less attractive and therefore this effect is expected. A clear advantage of the explicit simulation of the liquid-vapor interface over other techniques is the possibility of investigating the density profiles and interfacial properties such as the surface tension. These are discussed in the following.

Figure 1 shows the density profiles $\rho(z)$ at different temperatures. The insets represent typical configurations of the liquid-vapor interface of an ionic liquid where cavities can be observed. At high temperatures the ions associate into neutral dimers and larger size aggregates. In addition, the liquid-vapor interface shows to be very rough (see insets in Fig. 1). This has an effect on the thickness of the interface as we will see below. One important issue that has been raised in theoretical studies of the RPM density profiles refers to the asymmetry observed in the decay of the profiles to the liquid and vapor sides of the interface [19,20]. This decay is theory dependent and it is deemed to be a consequence of the different correlation lengths in the vapor and liquid phases. We have tried to analyze this question using the simulation density profiles by considering their derivatives. However, this analysis does not offer a definite answer on the decay of the density profiles. If there is a difference coming from the different correlation lengths in the liquid and vapor phases, this is not large enough to be reflected in the simulated density profiles.

Table I provides numerical estimates of the interfacial thickness of the RPM and SRPM models obtained using the "10-90" rule. As compared with water [24] and simple fluids [26], our results show that ionic systems exhibit a larger interfacial thickness [27]. It is important to point out that the surface tension of the ionic interface is much larger than that of simple liquids, and of the same order of magnitude than the water surface tension. These

TABLE I. Interfacial properties of the RPM and SRPM obtained in this work using HMD and MC simulations. The figure 0.0054_4 means 0.0056 ± 0.0004.

	RPM				SRPM			
k_BT/ϵ	$\rho_l\sigma^3$	$\rho_V\sigma^3$	δ/σ	$\gamma\sigma^2/\epsilon$	$\rho_l\sigma^3$	$\rho_V\sigma^3$	δ/σ	$\gamma\sigma^2/\epsilon$
0.0225[a]	0.630	···	1.5	0.0124_{15}	···	···	···	···
0.0275[a]	0.523	···	2.0	0.0099_{17}	···	···	···	···
0.035	0.412	0.0004	2.79	···	0.394	0.0003	2.67	···
0.036	0.395	0.0005	2.99	···	0.378	0.0003	3.07	···
0.038	0.365	0.0009	4.37	0.0054_4	0.349	0.0007	3.68	0.0056_4
0.040	0.332	0.0015	4.15	0.0049_4	0.319	0.0008	4.49	0.0047_5
0.042	0.301	0.0020	···	0.0040_4	0.285	0.0042	5.11	0.0031_5
0.043	0.289	0.0022	···	0.0030_4	0.272	0.0059	···	0.0022_5
0.044	0.272	0.0033	···	0.0023_6	0.256	0.0094	···	0.0013_4

[a]Monte Carlo simulations.

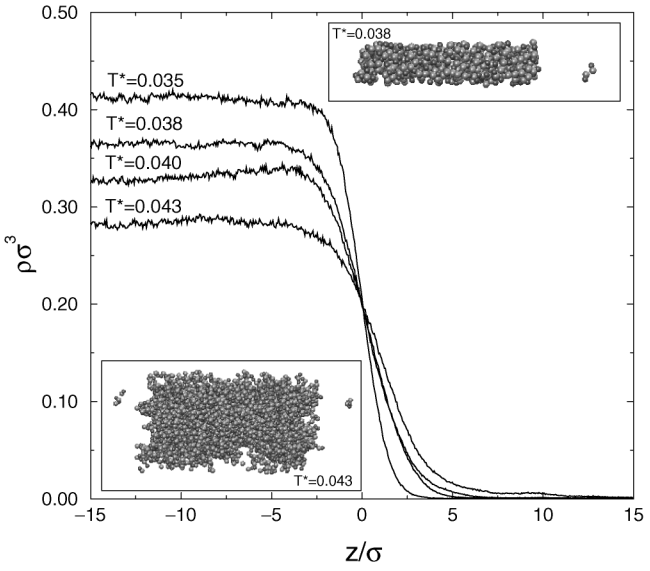

FIG. 1. RPM density profiles as a function of temperature. The insets show typical configurations for two temperatures.

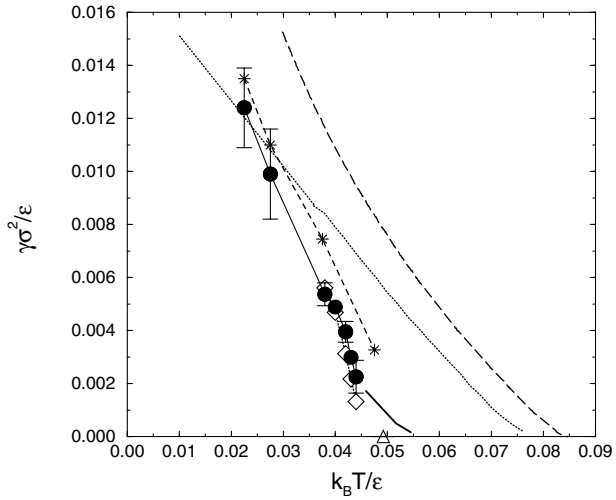

FIG. 2. Surface tension of the SRPM (open diamonds) and RPM (filled circles) as a function of temperature. Density functional theory results are shown with a dotted line (Ref. [18]) and a dashed line (Ref. [19]). The solid line represents AHNC-FL results from Ref. [20] and the stars represent cavity calculations from Ref. [25]. The critical point, taken from Ref. [7], is shown with open triangles.

differences in interfacial thickness, also observed in theoretical calculations [20], are an indication of the different structure of ionic liquid-vapor interface.

The surface tension of one liquid-vapor interface of the RPM was calculated by $\gamma = L_z[\langle P_{zz}\rangle - 0.5(\langle P_{xx}\rangle + \langle P_{yy}\rangle)]$ (see Refs. [22,24] for details), where $P_{\alpha\beta}$, ($\alpha, \beta = x, y, z$) is

$$VP_{\alpha\beta} = \sum_{i=1}^{N} m_i(\mathbf{v}_i)_\alpha(\mathbf{v}_i)_\beta + \sum_{i=1}^{N-1}\sum_{j>i}^{N}(\mathbf{r}_{ij})_\alpha(\mathbf{f}_{ij})_\beta, \qquad (2)$$

where m_i and $\mathbf{v}_i$ are the mass and the velocity of particle i, and $\mathbf{f}_{ij}$ is the force between a pair of particles. In the context of the RPM, the force is given by $\mathbf{f}_{ij}(r) = \mathbf{f}_{ij}^{(\mathrm{hs})}(r) + \mathbf{f}_{ij}^{(\mathrm{re})}(r) + \mathbf{f}_{ij}^{(\mathrm{rec})}(r) + \mathbf{f}_{ij}^{(\mathrm{trunc})}(r)$, where the superscripts are (hs), hard sphere; (re), real; (rec), reciprocal; and (trunc), truncation forces. For the soft model, $\mathbf{f}_{ij}^{(\mathrm{hs})}(r)$ is replaced by $\mathbf{f}_{ij}^{(\mathrm{soft})}(r)$.

The reduced surface tension, $\gamma^* = \gamma\sigma^2/\varepsilon$, calculated via the average components of the pressure tensor, is shown in Fig. 2 and numerical data collected in Table I. Good agreement is found between the RPM and SRPM models. The coexisting densities and surface tensions obtained have the same order of magnitude in both cases. This validates the HMD method and gives us confidence about the surface tension results for the RPM. In Fig. 2 surface tension results from density functional theories [18,19] are also shown. The critical properties, coexisting densities, and surface tension of the RPM are overestimated by these theories, which do not take into account that ions can associate to form small clusters. Recently, Weiss and Schröer [20] calculated interfacial properties of the RPM considering the ion-pair formation and interactions between the dipolar ion pairs and free ions using the approximate hypernetted chain relation in the Fisher-Levin theory (AHNC-FL). Their results are in good agreement with our simulation data. Nonetheless, we should point out that the use of this theory is restricted to a small range of temperatures ($T^* = 0.0459$–0.0545). We also compare the surface tension results with predictions from Monte Carlo simulations and cavity work of formation performed by some of us [25]. The cavity results represent a good approximation to the surface tensions, highlighting the importance of cavity formation in the vicinity of the binodal line.

The ratio of the RPM surface tension to the critical temperature $\tilde{\gamma} = \gamma^*/T_c^*$, obtained theoretically, has been compared with that of Lennard-Jones (LJ) fluids ($T_c^* \simeq 1.3$, $\rho_c^* \simeq 0.3$ in LJ units) and the large difference between both models has been highlighted as an intrinsic feature of ionic liquids [19]. Our results for the RPM reduced surface tension, where $\tilde{\gamma}_{\mathrm{RPM}}(T/T_c = 0.6) \simeq 0.3$, are of the same order of magnitude as those in simple fluids where $\tilde{\gamma}_{\mathrm{LJ}}(T/T_c = 0.6) \simeq 0.6$.

One important issue is to what extent the RPM is an accurate model to predict experimental surface tensions of ionic systems. Figure 3 compares the RPM surface tensions and experimental data of fused salts The surface tension of RPM has the same order of magnitude as that obtained in experiments for ionic salts involving ions of similar sizes, and the dependence of the surface tension with temperature is about the same for the available experimental data. Interestingly, the surface tension of

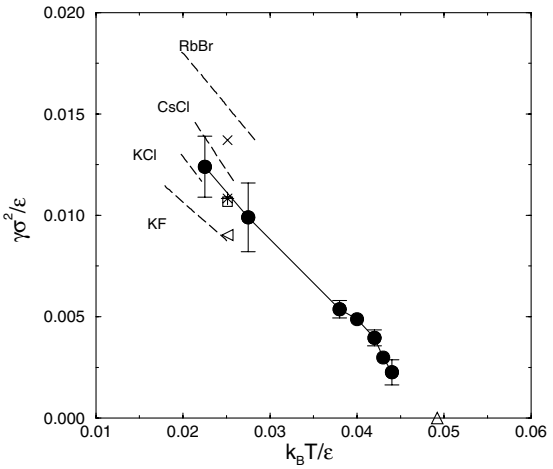

FIG. 3. Surface tension of the RPM as a function of temperature (filled circles) and experimental results for fused salts (dashed lines) taken from Ref. [18]. The cross and the star are simulation results from [16] for the fused salt potassium iodide (KI). The open triangle is a capillarity waves result from [17] for the same salt. The open square is an experimental result for KI [16]. Data taken from [16,17] are reduced with $\sigma = 3.49$ Å. The critical point, taken from Ref. [7], is shown as in Fig. 2.

the RPM at low temperatures has the same order of magnitude as that obtained using more realistic potential models including polarization terms [16,17]. It remains to be seen how sensitive the surface tension is to potential details and asymmetry in ion size, for instance. Work in this direction is in progress.

In summary, we have obtained the surface tension of the RPM using HMD and MC techniques in the liquid-vapor interface. The simulation results are compared with those obtained from theories that ignore or include the association of ions. A square-gradient theory [20], which includes association, predicts surface tensions in agreement with results from this work. The structure of an ionic interface is rather rough, and has a larger thickness than interfaces of simple liquids and water. Regarding the decay of the profiles to the bulk densities, we do not find significant differences between the vapor and liquid phases. These differences have been predicted recently using theoretical approximations. Our results indicate that they might be small or difficult to observe in the density profiles obtained from computer simulations. Finally, we find that the RPM, despite its simplicity, predicts surface tensions in excellent agreement with experimental data.

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[27] For $T/T_c = 0.779$, the interfacial thickness is $\delta_{\mathrm{LJ}} = 8.5$ Å [26], $\delta_{\mathrm{RPM}} = 13.5$ Å (this work), and $\delta_{\mathrm{water}} = 7$ Å [24]. For $T/T_c = 0.65$, $\delta_{\mathrm{LJ}} = 6.4$ Å, $\delta_{\mathrm{RPM}} = 8.5$ Å, and $\delta_{\mathrm{water}} = 5.1$ Å.