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Influence of a neutral component on the liquid–vapor coexistence and the surface tension of an ionic fluid

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ABSTRACT

We investigate the effect that a neutral component has on the liquid–vapor coexistence curve and the surface tension of an ionic fluid. Molecular dynamics simulations of a ternary mixture containing ions and neutral particles are performed. We found that the vapor branch is dominated by neutral particles and the liquid phase by ions. A comparison of our results and those of the soft primitive model (SPM) of a pure ionic fluid is made. For a fraction of neutral particles $x_0 = 0.2$, the density of the liquid phase is the same as that of the SPM, except for temperatures close to the critical point. As compared to the SPM, the surface tension takes the same values for low temperatures. For high temperatures, deviations of about 30% are observed. The estimated critical temperature and density of this ternary mixture are higher than those of the pure ionic fluid. In a preliminary study our results indicate that as x_0 increases the vapor density shifts to higher values, basically due to the concentration of neutral particles in that region. The liquid branch changes slowly until $x_0 = 0.5$, from that concentration of neutral particles, the liquid density decreases considerably. For high concentrations of the neutral component, the repulsive interactions dominate the system and the coexistence region is strongly reduced. Concerning the surface tension, we observed an increase with the fraction of neutral particles until $x_0 = 0.5$, from that value it reduces significantly, also as an indication of the strong repulsion in the system.

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1. Introduction

There are many fluids that can be classified as ionic fluids, among them we have electrolytes, molten salts, colloidal suspensions, polyelectrolytes, protein and ionic surfactant solutions and room temperature ionic liquids. All these systems contain charged particles or ions subjected to an overall electroneutrality condition whose electrostatic interactions have a strong influence on their behavior. These fluids are involved in several technological applications where surface or interfacial phenomena plays a key role [1]. A relevant property useful in there, is the surface or interfacial tension.

The addition of neutral particles to an ionic fluid can serve as a reference system in the description of more complex situations. For instance, a high concentration of neutral particles in a cell can affect the cellular functions, leading to different diseases such as cataract in eye lens and sickle cell anemia. This phenomenon, known as “macromolecular crowding”, has been studied in the context of the primitive model of electrolytes [2] and by using a soft repulsive potential between spheres representing the molecular environment [3]. The presence of neutral polymers or proteins in electrolytes or surfactant solutions can also be studied with a simplified model of ions and neutral particles. More exotic fluids such as magmas, which are silicate melt mixtures, can be well described as

mixtures of ions and neutral particles within a realistic picture of what fused rocks in the interior of the earth are [4].

There are in literature a few number of theoretical and simulation works addressing the effect that a neutral component produces on bulk thermodynamic and structural properties of ionic fluids [2,4–6]. However, until our knowledge, the effect that the addition of a neutral component has on the liquid–vapor coexistence and the surface tension of ionic fluids has not been analyzed before.

The aim of this work is to determine the effect that a neutral component has on the surface tension of an ionic fluid, described at the level of the primitive model.

This work is organized as follows: Section 2 describes the model and the calculated properties. Simulation details are given in Section 3. The liquid–vapor coexistence curve and the surface tension are presented and discussed in Section 4. Finally, conclusions are given in Section 5.

2. Model and calculated properties

We consider a ternary mixture of N_q charged soft spheres and N_0 neutral particles, all of equal diameter σ , immersed in a continuum solvent of dielectric constant ϵ_s . There are N_+ ions of charge $Z_+|e|$ and N_- of charge $Z_-|e|$, such that $N_- + N_+ = N_q$, and the total number of particles in the system is $N = N_q + N_0$. The fraction of neutral particles is then given by $x_0 = N_0/N$ and the mixture satisfies the electroneutrality condition, $\sum_{i=1}^N q_i = 0$, where $q_i = Z_i|e|$ is the charge

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of particle i . The interaction between any pair of particles separated on a distance $r = |\mathbf{r}_i - \mathbf{r}_j|$, regardless they are or not charged, is given by the soft primitive model (SPM) [7–9],

$$u_{ij} = A_s \left(\frac{\sigma}{r} \right)^n + \frac{1}{4\pi\epsilon_0\epsilon_s} \frac{Z_i Z_j e^2}{r}, \quad (1)$$

where ϵ_0 is the vacuum permittivity and e is the electron charge. We will consider a 1:1 system, so $Z_{\pm} = \pm 1$. The potential parameters for the soft repulsive interaction in Eq. (1) were chosen as in previous works [7,8], $A_s = -Z_+ Z_- e^2 / (4\pi\epsilon_0\epsilon_s\sigma)$ and $n = 225$.

Physical quantities were measured in units of length and energy given by σ and $E_{ref} = |u_{+-}(\sigma)| = |f(n)|A_s$, respectively, where $f(n) = [n^{n/(1-n)} - n^{1/(1-n)}] = -0.9718$ for $n = 225$. This SPM potential is very similar to the restricted primitive model (RPM) of ionic fluids [7], with the advantage that it is a continuous function of the distance and the molecular dynamics algorithm does not need the inclusion of collisions [10].

Several states within the liquid–vapor coexistence region were simulated. To obtain the densities of the liquid and vapor phases the average total density profile, obtained from the simulation, was fitted to a hyperbolic tangent function,

$$\rho(z) = \frac{1}{2}(\rho_L + \rho_V) - \frac{1}{2}(\rho_L - \rho_V) \tanh[(z - z_0)/d], \quad (2)$$

where ρ_L and ρ_V are the densities of the liquid and the vapor in the bulk phases, z_0 is the position of the Gibbs dividing surface, and d is a parameter that measures the thickness of the interface [11].

The surface tension was calculated by:

$$\gamma = \frac{L_z}{2} \left\{ \langle P_{zz} \rangle - \frac{1}{2} [\langle P_{xx} \rangle + \langle P_{yy} \rangle] \right\}, \quad (3)$$

where the factor 1/2 is due to the existence of two interfaces in the simulation method. The brackets $\langle \dots \rangle$ mean ensemble averages, L_z is the length of the simulation box in perpendicular direction to the interfaces, and $P_{\alpha\alpha}$ with $\alpha = x, y, z$, are the diagonal components of the pressure tensor, whose component $P_{\alpha\beta}$ is given by

$$P_{\alpha\beta} = \frac{1}{V} \sum_i^N m_i (\mathbf{v}_i)_\alpha (\mathbf{v}_i)_\beta + \frac{1}{V} \sum_{ij>1} (\mathbf{r}_{ij})_\alpha (\mathbf{f}_{ij})_\beta, \quad (4)$$

where m_i and \mathbf{v}_i are the mass and the velocity of particle i , respectively, $(\mathbf{f}_{ij})_\beta$ is the projection of the force between i and j in β -direction [12].

3. Technical details

We made use of the slab technique [13] to simulate the liquid–vapor coexistence of the fluid. The slab geometry consists in a parallelepiped simulation cell elongated in the direction z , having dimensions $L_x = L_y$ and $L_z > L_x$. A dense liquid slab of $N = 2000$ particles surrounded by vacuum was placed at the center of the simulation cell, we set $N_q = 1600$ ions, half of them positive and the other negative and $N_0 = 400$ neutral particles, which corresponds to a fraction of neutral particles $x_0 = 0.2$. A molecular dynamics simulation program at constant volume, number of particles and temperature was used to generate the time evolution of the system. To keep the temperature constant we used the scaling velocity method, with the velocity of the center of mass equal to zero in the starting configuration and during the dynamics to prevent wrong results [14]. We employed the velocity Verlet algorithm to integrate the classical Newton's equations of motion. As usual, minimum image convention and periodic boundary conditions (PBC) were applied in all directions [10]. In order to minimize surface area effects, introduced by the use of PBC, we set $L_x = 14\sigma$ and $L_z = 60\sigma$. These values are large

enough to avoid finite size effects in the calculation of surface tension [8,15]. The cut-off distance was $R_c = 4.0\sigma$ in all the simulations. The Ewald sum method [16–18] was used to calculate the electrostatic interactions with parameters $\kappa = 5.6/L_x$ and number of reciprocal vectors $(n_x, n_y, n_z) = (5, 5, 45)$. We checked that using this set of reciprocal vectors does not produce artificial contributions in the electrostatic energy and in the components of the pressure tensor, which could in turn lead to artifacts in the calculation of the surface tension [19–21].

The reduced time step, defined as $\Delta t^* = (E_{ref}/m\sigma^2)^{1/2} \Delta t$, being m as the mass of a particle was chosen as $\Delta t^* = 0.008$. The simulation runs consisted of at least 5×10^6 iterations produced in 100 blocks of 5×10^4 steps to calculate average properties, after 3×10^5 time steps of equilibration. The results are given in dimensionless units as follows: $z^* = z/\sigma$ for distance, $T^* = k_B T/E_{ref}$ for temperature, $\rho^* = \rho\sigma^3$ for density, and $\gamma^* = \gamma\sigma^2/E_{ref}$ for surface tension.

The density profiles of the species were calculated by dividing the z -axis in slabs of width $\Delta z = 0.05\sigma$ and volume $\Delta V = L_x L_y \Delta z$, then the density of particles of specie a in that volume, was calculated as $\rho_a(z) = N_a(z)/\Delta V$, being $N_a(z)$ the number of particles of species a . The total density profile was calculated in a similar way.

In order to investigate the effect that the concentration of neutral particles has on the properties here studied, we carried out a set of simulations with different fractions of neutral particles, x_0 . Besides the mixture with $x_0 = 0.2$, we considered systems with $x_0 = 0.5, 0.7$ and 0.9 , all with total number of particles fixed at $N = 2000$, then the number of positive and negative ions were adjusted to satisfy this total number N . Mixtures with $x_0 = 0.2$ and 0.5 were studied for the whole range of temperatures here explored, whereas the systems with $x_0 = 0.7$ and 0.9 were simulated just at $T^* = 0.0309$. The rest of the parameters used in the simulations were the same as those previously described.

4. Liquid–vapor coexistence and surface tension

The total average density profile $\rho(z)$ of the ternary mixture with fraction of neutral particles $x_0 = 0.2$ is presented in Fig. 1 at different temperatures. As temperature increases the density of the liquid decreases appreciably, however the density of the vapor increases very slowly. This almost unaffected vapor density is achieved by increasing the volume occupied by the liquid region in the simulation cell, resulting in a lower density as the liquid expands, as can be observed in the profiles presented in Fig. 1.

Fig. 2 shows the average density profiles of each species at $T^* = 0.036$ for the same mixture as in Fig. 1. As expected, the density profile of the positive and negative charged species is the same. Neutral particles

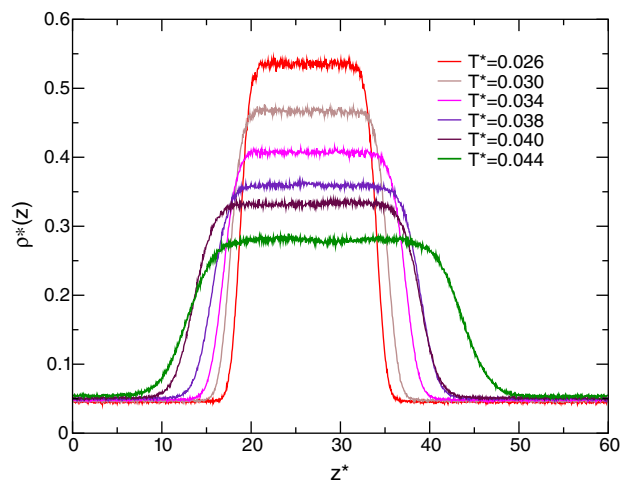


Fig. 1. Total density profile of the system with $x_0 = 0.2$ as a function of temperature, shown from top to bottom.

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