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Molecular model of fused salts near an electrode

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We study the charged–hard-sphere model of a fused salt near a planar electrode, using a density-functional theory of inhomogeneous electrolytes. The results at relatively high temperatures show an oscillating charge distribution near the electrode, suggesting that near solid-liquid coexistence, the electrode is "coated" by a few atomic layers of the solid phase, analogous to wetting phenomena at liquid-vapor coexistence. At lower temperatures, we observe the growth of a macroscopically large ordered (solidlike) phase that is separated from the bulk fluid by an interface that extends over many molecular layers. Among other things this result shows, for the first time in the literature, that a density-functional theory is capable of producing a thermodynamically stable, ordered phase without the need of putting in any crystallographic symmetry at forehand.

I. INTRODUCTION

The system of a molten salt near an electrode is of interest from a theoretical point of view, since it is of fundamental importance in chemical physics; and it is of interest from a technological point of view, since the wetting of electrodes by fused salts is of vital importance in heterogeneous catalysis.[1] In these technological applications, the wetting of the solid by the liquid is determined by the solid-liquid, the liquid-vapor, and the solid-vapor surface tensions that in turn follow from the density distribution of the fluid near the respective interfaces. To calculate these density distributions on a statistical mechanical footing, one has to simplify reality to a mathematical model. One model that has been used frequently in the study of homogeneous liquids, is the charged–hard-sphere model, in which the molecules of the fluid are replaced by hard spheres that interact at long distances by a $1/r$ potential.[2] The quantitative properties of this model do not seem to match the experimental data of fused salts very well, however, and this has led to the introduction of some more elaborate models.[3]

However, since the theory of inhomogeneous fused salts is far from developed at present, we wish to study the simple charged–hard-sphere model near a hard planar wall first, before the more elaborate models are analyzed. Recently, Li and Mazo[4] have studied this model in the generalized mean-spherical approximation (GMSA) and found damped oscillations in the charge density as a function of the distance from the wall. Since this theory describes the density as a perturbation from a fixed reference density, it is incapable of describing two-phase coexistence, and moreover, since it is a linear theory, the damping of the charge oscillations near the wall must equal the bulk GMSA property that has been put into the model. The advantage of the GMSA, naturally, is the possibility of finding analytic solutions since it is a linear theory, but the price to pay for this advantage is the need of putting in the surface sum rules by hand.

A completely different type of theory is the density-functional method.[5] This theory is based on a functional expansion of the free energy of an inhomogeneous liquid about that of a locally optimized reference state,[6] and has been introduced by one of us[7] for the inhomogeneous electrolyte problem. Surface sum rules come out automatically in such a model, and two-phase coexistence is possible,[8] i.e., it is not at forehand excluded. In the present paper we use this theory to calculate the density distribution of a fused salt near a planar electrode, at some values of the temperature and the surface charge at the electrode. For small values of the surface charge and at high temperature we find the charge oscillations near the electrode to damp out at the length scale of the bulk fluid correlation length, just as a linear theory would predict. As solid-liquid coexistence is approached, and the surface charge is increased, we find these oscillations to damp out more slowly, which points to what we propose to call "coating" of the electrode by the solid phase, on the analogy of wetting phenomena at liquid-vapor coexistence. Before presenting these results in Sec. III, we briefly discuss the density-functional theory in Sec. II. Our conclusions and some points of discussion are summarized in Sec. IV.

II. THE DENSITY-FUNCTIONAL THEORY

In the charged–hard-sphere model, the particles interact with the simplest possible pair potential to describe electrolytes. The repulsive part of the potential is taken to be a hard-sphere interaction, where all particles have the same diameter R. This potential is given by

$$V_{ij}(r)=\begin{cases}\infty \quad \text{if } r<R\ , & \text{(1a)}\\ \dfrac{1}{4\pi\varepsilon}\dfrac{q_iq_j}{r} \quad \text{if } r>R\ , & \text{(1b)}\end{cases}$$

where $\varepsilon=\varepsilon_0\varepsilon_r$ is the dielectric constant of the medium, and q_i is the charge of particle type i in SI units. The thermodynamic state in this model is completely determined by two dimensionless parameters, namely, the reduced density

$$\rho^* = \rho R^3 \tag{2}$$

and the reduced temperature

$$T^* = 4\pi \varepsilon k T R / q^2 , \tag{3}$$

where q is the unit of charge, and k is Boltzmann's constant. Instead of the reduced temperature, a dimensionless charge Q_i or coupling constant Q will often be used here. They are defined by

$$Q_i = \frac{q_i}{\sqrt{\varepsilon k T R}} = z_i \left[\frac{4\pi}{T^*} \right]^{1/2} , \tag{4}$$

where z_i is the charge of species i in elementary charge units and $Q = Q_1$ $(z_1 = 1)$. In the sequel we denote the positive particles with the subscript 1 $(z_1 = 1)$ and the negative ones by the subscript 2 $(z_2 = -1)$.

To describe the charge distribution near a charged wall in an elaborate manner, we study a theory in which the density is described by a large number of very thin layers parallel to the wall. The density in each layer is a free variable that must be determined by the theory. These variables follow from the condition that the grand potential of the system must be minimal; for a system containing two types of particles having dimensionless charges Q and $-Q$ (or $Q_i = z_i Q$, where $z_i = \pm 1$), this grand potential is, in the presence of an external electrostatic field $\phi^{\text{ext}}(\mathbf{r})$, given by[7]

$$\begin{aligned} \beta\Omega = \int \sum \rho_i(\mathbf{r})[\ln(\rho_i(\mathbf{r})\lambda_i^3) - \mu_i - 1 + \Delta f_S(\{\rho^0\}) + z_i\, \Delta f_D(\{\rho^0\}) + Q_i(\phi^{\text{ext}}(\mathbf{r}) + \tfrac{1}{2}\phi^{\text{int}}(\mathbf{r}))]d^3r \\ + \int d^3r \int d^3r' \sum_{i,j} \rho_i(\mathbf{r}) G_{ij}(\mathbf{r}-\mathbf{r}';\rho^0(\mathbf{r}))(\rho_j(\mathbf{r}') - \rho_j^0(\mathbf{r})) , \end{aligned} \tag{5}$$

where $\beta = 1/kT$, and where the following auxiliary functions are used. Firstly, the densities ρ_i^0 are coarse-grained densities that vary slowly in space, and that are used to define an optimized local thermodynamic state of reference. We denote $\sum_i \rho_i^0$ by ρ^0; the definition of these reference densities will be given later. Secondly, the functions Δf_S and Δf_D are the relevant expressions for the excess free energy per particle of the reference state:

$$\Delta f_S = -\sum_i \rho_i^0 \int_0^1 d\zeta \int d^3r\, G_S(\zeta\rho^0) , \tag{6a}$$

$$\Delta f_D = -\sum_i z_i \rho_i^0 \int_0^1 d\zeta \int d^3r\, G_D(\zeta\rho^0) , \tag{6b}$$

where G_S and G_D are "sum" and "difference" couplings, from which the coupling matrix follows as

$$G_{ij} = \begin{bmatrix} G_S + G_D & G_S - G_D \\ G_S - G_D & G_S + G_D \end{bmatrix} . \tag{7}$$

The field $\phi^{\text{int}}(\mathbf{r})$, finally, is the electrostatic field due to the charges of the fluid; it is by definition the solution of Laplace's equation,

$$\Delta\phi^{\text{int}}(\mathbf{r}) = -\sum_i Q_i \rho_i(\mathbf{r}) . \tag{8}$$

To find the reference densities, we require the free energy to be stationary under variations with respect to the variables ρ_i^0. Since in Eq. (5) we have taken coupling functions G_{ij} that do not depend on the difference reference density $\rho_1^0 - \rho_2^0$, this requirement does not determine all reference densities, but following the approximation introduced by one of us,[7] we take

$$\rho_1^0 + \rho_2^0 = \langle \rho_1 + \rho_2 \rangle_S , \tag{9a}$$

$$\rho_1^0 - \rho_2^0 = \langle \rho_1 - \rho_2 \rangle_D , \tag{9b}$$

where $\langle a \rangle_{S/D}$ stands for $\int G'_{S/D} a(r') d^3r' / \int G'_{S/D} d^3r'$, with $G'_{S/D} = \partial G_{S/D}(r - r';\rho)/\partial\rho$. The reference densities therefore are fixed when the coupling functions are known. Following the model defined earlier,[7] these are given by

$$G_S(r;\rho^0) = E(r;\rho^0) + \int_0^1 C^{\text{PY}}(r;\zeta\rho^0)\zeta\, d\zeta , \tag{10a}$$

$$G_D(r;\rho^0) = \frac{1}{2} \left[C_D^{\text{MSA}}(r;\rho^0) + \frac{Q^2}{4\pi r} \right] . \tag{10b}$$

The function E in (10a) is defined as

$$E(r;\rho) = \frac{\pi}{6}\theta(r-1)\frac{\eta^2}{(1-\eta)^3}\frac{e^{-2\pi(r-1)}}{r}\cos(2\pi r) , \tag{11}$$

where $\eta = \pi\rho/6$ is the packing fraction, and C^{PY} is the Percus-Yevick solution to the hard-sphere direct correlation function. The expression, integrated with respect to the density, that is needed in (10a) can be found in the literature.[6] The function C_D^{MSA} in Eq. (10b) is the mean-spherical approximation to the difference direct correlation function $(C_{++} - C_{+-})/2$ which is calculated by Waisman and Lebowitz.[9]

III. RESULTS

In the present article we use this theory to calculate the density distribution of a fused salt near a planar electrode. The set of parameters that we use applies to molten KCl and is given by the temperature $T = 1500$ K and the particle diameter $R = 3.14$ A. The value of ε_r has been varied from $\varepsilon_r = 1$ to $\varepsilon_r = 10$ in order to study the effect of the polarizability of the ions. The equilibrium density in the bulk of the liquid, i.e., far away from the electrode, has been fixed at $\rho = \rho_+ + \rho_- = 0.669$, where the hard-sphere diameter has been used as the unit of length. For this set of parameters, the dimensionless coupling constant varies from $Q = 21$ for a nonpolarizable salt to $Q=6.7$ at $\varepsilon_r=10$, and the Debeye-Hückel inverse screening length that is given by $x=Q\sqrt{\rho}$ varies from $x=17$ to $x=5.5$. This range of parameters may alternatively be viewed as a temperature variation from $T^*=0.028$ to $T^*=0.28$, or from $T=1500$ K to $T=15\,000$ K at $\varepsilon_r=1$.

This ionic liquid is confined between two hard planar walls that are situated at $z=0$ and at $z=\Lambda$, where the system size Λ is chosen sufficiently large. The repulsive interaction between fluid and walls is described by the imposed boundary conditions, namely, $\rho_i(z)=0$ for $z<\frac{1}{2}$ and for $z>\Lambda-\frac{1}{2}$. The electrostatic interaction with the walls is described by the introduction of the external field $\phi^{\text{ext}}(z)$ that is given by $\nabla\phi^{\text{ext}}(z)=Q\sigma^*$ and $\phi^{\text{ext}}(\Lambda)=0$. The boundary conditions used for the internal field are $\nabla\phi^{\text{int}}(0)=0$ and $\phi^{\text{int}}(\Lambda)=0$; thus we describe a finite system with a surface charge $-\sigma=-\sigma^*q/R^2$ at the left wall, and with a grounded conductor at the right wall. We have performed calculations for $\sigma^*=0.1, 0.2, 0.3$ and for $\sigma^*=0.4$.

To study the behavior of the system for a given surface charge, as a function of the reduced temperature, we calculated the density profiles for the given parameters at $\varepsilon_r=2$, 4, and 10, at the surface charge $\sigma^*=0.40$. These density distribution functions have been plotted in Fig. 1, where the solid curves give the counterion densities, and the dashed curves give the coion densities. We observe the formation of an oscillating layer near the electrode, which is of increasing thickness with increasing coupling. The occurrence of these oscillations is in line with the results of Monte Carlo simulations by Heyes and Clarke on charged soft spheres,[10] and with the charge oscillations observed by Larsen[11] in the bulk correlation function of charged hard spheres. For the smallest couplings $\varepsilon_r=10$ and $\varepsilon_r=4$ (these values correspond to a high reduced temperature), we find the oscillations to decrease exponentially with a decay rate that matches the MSA correlation length. At $\varepsilon_r=2$, however, we find the first few oscillations to decay slower than expected on account of the MSA correlation length, unless the surface charge is reduced to $\sigma^*=0.1$. For higher surface charges and for a low value of ε_r, we also find the local sum reference density to be increased over several molecular layers near the wall.

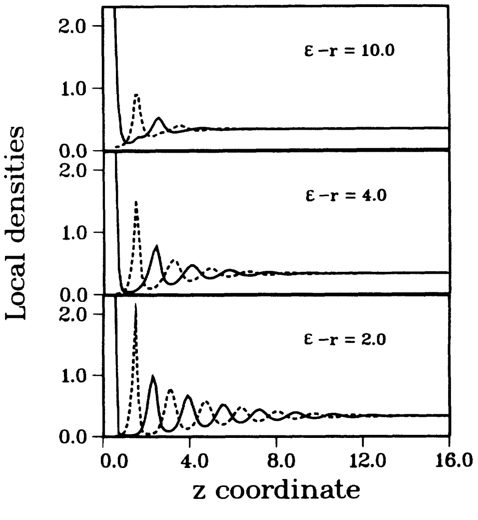

FIG. 1. The density profiles of a fused salt near an electrode of surface charge $\sigma^*=0.5$ for various dielectric constants.

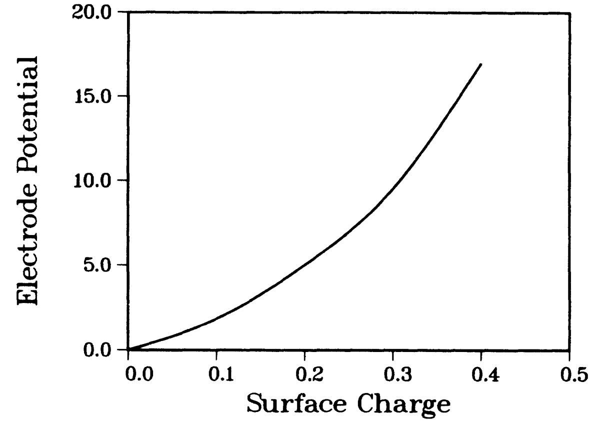

FIG. 2. The dimensionless potential $\beta q\psi$ of the electrode in the presence of a fused salt with $\varepsilon_r=2.0$ as a function of the surface charge σ^*.

The validity of the present theory may be tested by comparing its predictions with experimentally accessible quantities. One observable property of the described system is the potential of the electrode as a function of the surface charge. To find this function, we have also varied the surface charge for a salt of $\varepsilon_r=2$. The potential at $z=0, \beta q\psi_0=Q[\phi^{\text{ext}}(0)+\phi^{\text{int}}(0)]$, is given in Fig. 2 for this system. This experimentally observable quantity, however, is only indirectly related to the density distribution. A more direct experimental observation of the density profile would be very desirable, and can in principle be performed using ellipsometry or related techniques. These methods may provide information about the thickness of the layer by means of the coverage of the electrode by the salt. For an electrode situated at $z=0$, we define the nth moment of the adsorbed layer of species i as

$$\Gamma_i^n=\int_0^\infty[\rho_i(z)-\rho_i(\infty)]z^n dz\ , \tag{12}$$

where the fluid extends to infinity. In fact, Γ_i^0 is the observable that is usually named "coverage," and the ratio Γ_i^1/Γ_i^0 is a measure of the thickness of the adsorbed layer of species i. For the systems that have been discussed, we have compiled these moments of the layer in Table I.

TABLE I. Some moments of the adsorbed layer of a fused salt at the electrode.

σ^*	ε_r	Γ_1^0	Γ_1^1	Γ_2^0	Γ_2^1
0.1	2.0	0.005	0.031	−0.095	0.025
0.2	2.0	0.089	0.083	−0.111	0.060
0.3	2.0	0.182	0.165	−0.118	0.107
0.4	2.0	0.278	0.218	−0.122	0.125
0.4	4.0	0.225	0.117	−0.175	−0.031
0.4	10.0	0.184	0.090	−0.216	−0.024

A completely different situation from the one that is outlined above, occurs if the dielectric constant is reduced to $\varepsilon_r = 1$. To describe the results here, we need to explore the question of how the density profiles are calculated in some more detail. The method we use to calculate the density distribution is an iterative one, where we start with a uniform density, and change this profile by taking steps along the steepest descent of the grand potential, with a step size that is proportional to the gradient of the grand potential in function space. This way, the minimum of the grand potential is reached in a manner very similar to the way a real system equilibrates, and thus the study of the density profile as a function of the number of iteration steps gives insight into the nonequilibrium properties of the system.

When this procedure is used to calculate the density profile at $\varepsilon_r = 1$ and $\sigma^* = 0.1$, one observes the growth of a large solidlike ordered layer adjacent to the electrode. The thickness of this layer increases proportional to the number of iterations, and we did not observe any indication that the growth velocity of this ordered structure slows down after a plateau in the oscillation amplitude was reached (see Fig. 3). We thus conjecture the solid phase to be the stable one in this case, and interpret this observation as the growth of the solid salt from its undercooled melt. To test whether the observed ordered structure indeed corresponds to an intrinsic minimum of the grand potential, we also calculated the density profiles for a surface charge density $\sigma^* = 0.2$ from a uniform start. After the same number of iterations, we obtained density profiles that only differ from those that are given in Fig. 3 for the first two (solid) layers adjacent to the wall. As expected, both the amplitude of the density oscillations at the plateau, and the envelope of the solid-liquid interface reproduce exactly.

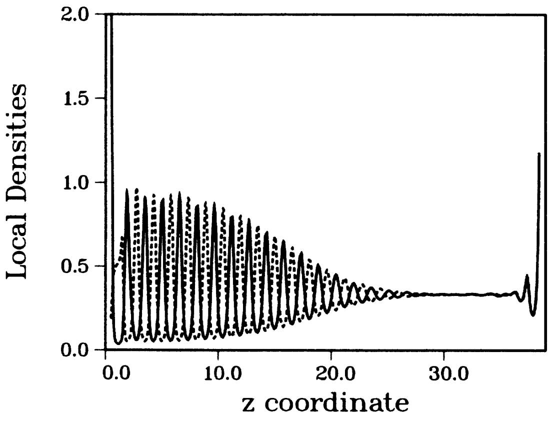

FIG. 3. A typical density profile at growth conditions. The surface charge equals $\sigma^* = 0.1$ and $\varepsilon_r = 1.0$.

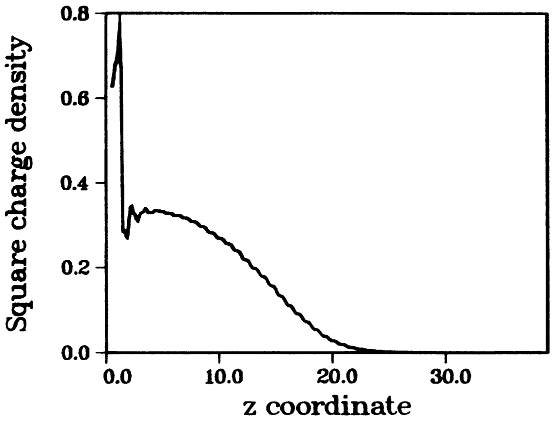

FIG. 4. The square density order parameter for the density profile given in Fig. 3.

To discriminate between the solid and the liquid, one could study the local sum reference density: in the solid phase we find an increase in the coarse-grained density by 3% relative to the density in the fluid phase. This increase seems realistic in comparison with experimental systems, but its small value causes problems to trace the solid. To distinguish the ordered phase from the bulk liquid, we therefore suggest the introduction of the "square density" $S(z)$ as an order parameter that we define by

$$S(z)=\frac{1}{\Delta}\int_{z-\Delta/2}^{z+\Delta/2}[\rho_1(z)-\rho_2(z)]^2\,dz\ , \tag{13}$$

where Δ is the wavelength of the oscillations at the plateau of the ordered structure. This order parameter in practice changes by a factor of 10^4 between the solid and the liquid phases. This function is given in Fig. 4, which shows a very smooth interface between the solid and the liquid. The interface involves many layers, as is expected in the Cahn picture of a solid-liquid interface.[12]

IV. DISCUSSION

Using a density-functional method, the density distribution of a fused salt has been calculated in the neighborhood of a charged electrode. We find this distribution to show oscillations in the local charge density by the formation of layers of alternating charge. The occurrence of these charge oscillations is in line with the expectation, given the observed charge oscillations that appear in the charged-soft-sphere model,[10] and in the correlation function of the charged-hard-sphere model.[11] Within our theory, the system tends to freeze between $T^* = 0.028$ ($\varepsilon_r = 1$) and $T^* = 0.056$ ($\varepsilon_r = 2$), but the actual value of the freezing temperature in this theory is strongly influenced by the simple MSA direct correlation function for which we used the theory.[7] One cannot expect this simple direct correlation function to lead to an accurate prediction of the freezing temperature.

What is of importance at this point, however, is the fact that within our model, the temperature of the system at $\varepsilon_r = 2$ is above, but close to, the freezing temperature. Thus the increased density, and the reduced decay rate of the charge oscillations at $\varepsilon_r = 2$ near the wall, may be interrelated in the following manner. Due to the presence of the wall, the system which is already close to solid-liquid coexistence is pulled away from the stable liquid phase into the metastable solid phase. Thus the wall is "coated" by a few molecular layers of the solid phase on the analogy of wetting phenomena at liquid-vapor coexistence. Questions as to whether we have to indeed consider a "precoating" or a "critical coating" transition are at present unclear. A more thorough study at this point, using Monte Carlo and density-functional techniques seems advisable.

With respect to our ordered solution at $\varepsilon_r = 1$, we wish to remark that in our theory the density parallel to the wall has been averaged out at forehand. This procedure excludes the description of a lateral structure, hence the ordered solution lacks a real three-dimensional crystalline symmetry. Several quantitative features of the interface, however, are expected to not be influenced much by this neglect of the lateral structure. Thus we predict a Cahn-like interface for the {111} face of a simple salt in contact with its melt.[12] This interface excludes the presence of facets in this orientation, which is in line with the observations. Indeed the only faces observed on alkali halogenides, grown from their melts, are the {100} faces.[13] The other faces are absent, and the crystals generally appear to be round, in agreement with the present theory.

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