Simple theory for oscillatory charge profile in ionic liquids near a charged wall

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Abstract

The mesoscopic field theory for ionic systems [A. Ciach and G. Stell, J. Mol. Liq. 87, 255 (2000)] is extended to the system with charged boundaries. A very simple expression for the excess grand potential functional of the charge density is developed. The size of hard-cores of ions is taken into account in the expression for the internal energy. The functional is suitable for a description of a distribution of ions in ionic liquids and ionic liquid mixtures with neutral components near a weakly charged wall. The Euler-Lagrange equation is obtained, and solved for a flat confining surface. An exponentially damped oscillatory charge density profile is obtained. The electrostatic potential for the restricted primitive model agrees with the simulation results on a semiquantitative level.
I. INTRODUCTION

Ionic systems have been studied for decades. At the beginning, the main interest concerned diluted systems or electrolytes. The theory of such systems is very well developed, and one of the main contributors was Lesser Blum. His works on the mean spherical approximation (MSA) and its various extensions applied to ionic solutions, especially Refs. [1, 2], have been very influential. Apart from the bulk properties, studies focused on the distribution of ions near a charged wall. In the works [3, 4] by Douglas Henderson and Lesser Blum, exact relation for the contact value of the wall-fluid correlation function, and exact asymptotic expression for large distances from the wall of this function are given; in addition, MSA results for this system are presented. The liquid-matter theories, however, are rather difficult.

Properties of electrolytes near a charged surface are very well described by the elegant and simple theories of the mean-field (MF) type, in particular by the Debye-Hueckel (DH) theory [5–7]. Ions in these theories are treated as point-like charges. In the case of ionic liquids, however, these theories cannot correctly predict the oscillatory decay of the charge density as the separation from the weakly charged surface increases [2–11]. It is commonly assumed that the monotonic decay of the charge density results from the MF character of the theories. However, for large densities of the ions the finite size of their cores starts to play an important role. The hard-core packing is carefully taken into account in the density functional theory (DFT) [12], that is of the MF type. The DFT correctly predicts the oscillatory decay of the density profile in neutral fluids confined by solid walls [13]. An oscillatory decay of the charge density near a confining surface is a natural consequence of the oscillatory decay of the densities of the anions and the cations. A role similar to steric repulsions is played by the forbidden multiple occupancy of lattice sites in lattice models. As a consequence, damped oscillations of the charge were obtained in a one-dimensional lattice Coulomb gas by exact calculations [14].

The decay of the excess density near a wall mimics the decay of the density-density correlation function in the bulk, up to the amplitude and phase depending on the properties of the surface. In the theory developed in Ref. [15–17], oscillatory decay of correlations was obtained on the MF level [16, 17]. This theory is a kind of simplistic DFT, combined with the field-theoretic way of incorporating fluctuations beyond its MF version. The finite size
of the cores of ions is taken into account in the calculations of the electrostatic energy, i.e. the contributions from the overlapping cores are not included. As the decay of the charge density near a wall mimics the decay of the charge-density correlations in the bulk, one can expect that in this MF theory the oscillatory decay of the charge density should be obtained. Such an expectation is explicitly written at the end of Ref.[16]. Unfortunately, the correlation functions were obtained in the Fourier representation, and in the case of the broken translational symmetry the real-space representation is required to obtain the charge-density profile.

In this work we propose an approximate version of the theory developed in Ref.[15] that can be applied to confined systems. We develop a functional of the charge- and number density of ions that has a very simple form. In the lowest-order approximation, the functional depends only on the local charge density, and has a form of a single integral in real space. For this functional we obtain the Euler-Lagrange (EL) equation for the charge density. This EL equation can be easily solved analytically, and the theory can be systematically improved. Its advantage is a simplicity and possibility of obtaining approximate analytical expressions for the charge profile near the charged wall.

In sec.2 we shortly summarize the theory developed for ionic systems in the bulk. In sec.3 we develop and solve the EL equation. Discussion and conclusions are included in sec.4.

II. SHORT SUMMARY OF THE THEORY FOR THE BULK SYSTEM

We consider a mixture of spherical cations with a diameter \( \sigma_+ \) and a charge \( e_+ \), and spherical anions with a diameter \( \sigma_- \) and a charge \( e_- = -|e_-| \) dissolved in a structureless solvent with the dielectric constant \( \epsilon \). The local dimensionless number densities of the cations and the anions are denoted by \( \rho_+ (r) \) and \( \rho_- (r) \), respectively. For clarity of presentation we restrict ourselves to the anion-cation symmetric case, with \( \sigma_+ = \sigma_- = \sigma \) and \( e_+ = |e_-| = e \), where \( e \) is the elementary charge. In general, the symmetrical case corresponds to the Restricted Primitive Model (RPM) with addition of the specific short-range (SR) interactions [18]. In the RPM, the interactions consist of the steric repulsion for overlapping spherical cores and of Coulomb interactions between point charges in the centers of the cores. The more general case of size- and charge asymmetric ions is described in Ref.[19, 20].
We introduce local dimens \( A, \theta \), ionless charge and number densities at \( r \) by

\[
\phi(r) = \rho_+(r) - \rho_-(r) \tag{1}
\]

and

\[
\rho(r) = \rho_+(r) + \rho_-(r). \tag{2}
\]

In the bulk homogeneous phase \( \phi = 0 \) and \( \rho(r) = \rho_0 \).

The internal energy consists of the electrostatic energy, \( U_{RPM} \), and the energy associated with the SR interactions, \( U_{SR} \), \( U = U_{RPM} + U_{SR} \), with

\[
U_{RPM}[\phi] = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi(\mathbf{r}_1)V_C(\mathbf{r})g(\mathbf{r})\phi(\mathbf{r}_2), \tag{3}
\]

where \( r = |\mathbf{r}_1 - \mathbf{r}_2| \), \( V_C(r) \) is the Coulomb potential and \( g(r) \) is the pair distribution function. A very rough approximation for the pair distribution function is

\[
g(r) = \theta(r - 1). \tag{4}
\]

In (4) and in the following, length is measured in \( \sigma \) units (i.e. we put \( \sigma \equiv 1 \)). In the above approximation, \( g(r) \) vanishes for \( r < 1 \) as it should, and is equal to unity for \( r > 1 \), i.e. it has a proper behavior for large \( r \). It is convenient to introduce the dimensionless function

\[
V^*(r) = \frac{\epsilon \sigma}{e^2} V_C(r)g(r) = \frac{\theta(r - 1)}{r} \tag{5}
\]

and the dimensionless temperature

\[
T^* = \frac{1}{\beta^*} = \frac{\epsilon \sigma}{e^2} k_B T, \tag{6}
\]

where \( k_B \) and \( \epsilon \) are the Boltzmann and the dielectric constant, respectively. With the above definitions, \( \beta V_C(r)g(r) = \beta^* V^*(r) \).

In Fourier representation \( V^* \) has the form

\[
\tilde{V}^*(k) = \frac{4\pi \cos(k)}{k^2}. \tag{7}
\]

Note that for \( k > \pi/2 \) we have \( \tilde{V}^*(k) < 0 \), and the charge waves with such wavenumbers, \( \phi(z) \propto \cos(kz) \), are energetically favoured compared to \( \phi = 0 \). \( \tilde{V}^*(k) \) assumes a minimum for \( k = k_b \approx 2.46 \) in \( \sigma^{-1} \)-units, and the wavelength of the most probable charge-density waves is \( 2\pi/k_b \approx 2.5 \) (in \( \sigma \)-units). The length scale of the charge oscillation is determined
by the size of the impenetrable cores. In our theory, the contribution to the electrostatic energy coming from overlapping cores is not included because of the \( \theta \)-function present in Eq.\( [3] \) (see also Eq.\( [3] \)).

For the symmetrical case, the contribution to the internal energy associated with the SR interactions can be written in the form

\[
U_{SR}[\phi] = \frac{1}{2} \int dr_1 \int dr_2 \phi(r_1) K_\phi(r) \phi(r_2) + \frac{1}{2} \int dr_1 \int dr_2 \rho(r_1) K_\rho(r) \rho(r_2)
\]

where \( K_\phi \) and \( K_\rho \) denote the product of the interaction potential and the pair distribution function. We introduce dimensionless SR potentials by \( \beta^* K_\phi = \beta K_\phi \) and \( \beta^* K_\rho = \beta K_\rho \), with \( \beta^* \) defined in \( [6] \).

Let us consider the excess grand potential associated with particular local inhomogeneities, \( \phi(r) \) and \( \eta(r) = \rho(r) - \rho_0 \),

\[
\Delta \Omega[\phi, \eta] = \Omega[\phi, \rho_0 + \eta] - \Omega[0, \rho_0],
\]

where

\[
\Omega[\phi, \rho] = U[\phi, \rho] - TS[\phi, \rho] - \mu \int dr \rho(r),
\]

with \( U, S, T, \mu \) denoting the internal energy, entropy, temperature and the chemical potential respectively. When the grand potential assumes a minimum for \( \phi = 0 \) and \( \rho = \rho_0 \), then the first functional derivatives of \( \Omega \) vanish, and terms linear in \( \phi \) and \( \eta \) are absent in \( \beta \Delta \Omega[\phi, \eta] \).

The excess grand potential takes the form

\[
\beta \Delta \Omega[\phi, \eta] = \beta \Delta \Omega_G[\phi, \eta] + \beta \Delta \Omega_{ho}[\phi, \eta]
\]

where the part containing the second-order terms in \( \phi \) and \( \eta \) is

\[
\beta \Delta \Omega_G[\phi, \eta] = \frac{1}{2} \int dk \hat{\phi}(k) \tilde{C}_{\phi\phi}(k) \hat{\phi}(-k) + \frac{1}{2} \int dk \hat{\eta}(k) \tilde{C}_{\eta\eta}(k) \hat{\eta}(-k)
\]

with

\[
\tilde{C}_{\phi\phi}(k) = \rho_0^{-1} + \beta^* (\tilde{V}^*(k) + \tilde{K}_\phi^*(k)),
\]

\[
\tilde{C}_{\eta\eta}(k) = \gamma_{0,2} + \beta^* \tilde{K}_\rho^*(k).
\]

We use Fourier representation for this part of \( \Delta \Omega \) for convenience. The terms of higher-order in \( \phi \) and \( \eta \) are included in the local term

\[
\beta \Delta \Omega_{ho}[\phi, \eta] = \sum_{m,n} \gamma_{2m,n} \frac{\gamma_{2m,n}}{(2m)!n!} \int dr \phi^{2m}(r) \eta^n(r).
\]
In the summation in (15), only terms with $2m + n > 2$ are included, and
\[ \gamma_{2m,n} = \beta \left. \frac{\partial^{2m+n} f_h}{\partial \phi^{2m} \partial \rho^n} \right|_{\phi=0, \rho=\rho_0}. \] (16)

To obtain Eqs.(12)-(15) from (10), we have approximated $-T \Delta S$ by the excess free energy of the hard-spheres mixture in the local density approximation. For the free-energy density of hard spheres, $f_h(\phi, \rho)$, we may assume the Percus-Yevick or Carnahan-Starling (CS) approximation.

Note that in (9), the excess of the grand potential associated with a particular local deviation form the average values of $\phi$ and $\eta$ is considered. In the presence of thermal fluctuations, all such deviations must be taken into account with a proper weight to obtain the true grand potential. In such a case the charge-charge correlation function is defined by,
\[ \tilde{G}_{\phi\phi}(k) \equiv \langle \tilde{\phi}(k)\tilde{\phi}(-k) \rangle = \frac{\int D\phi D\eta \tilde{\phi}(k)\tilde{\phi}(-k)e^{-\beta \Delta \Omega[\phi,\eta]}}{\int D\phi D\eta e^{-\beta \Delta \Omega[\phi,\eta]}}. \] (17)

It reduces just to
\[ \tilde{G}_{\phi\phi}^0(k) = 1/\tilde{C}_{\phi\phi}^0(k) \] (18)
when $\beta \Delta \Omega_{ho}[\phi, \eta]$ is neglected in (11). The density-density correlation function $G_{\eta\eta}$ is defined in an analogous way, and when $\beta \Delta \Omega_{ho}[\phi, \eta]$ is neglected in (11), it reduces to $\tilde{G}_{\eta\eta}^0 = 1/\tilde{C}_{\eta\eta}^0$.

In the rest of this work we limit ourselves to the pure RPM for clarity. Generalization to the RPM+SR system is straightforward. In the RPM, $\tilde{C}_{\phi\phi}^0(k)$ is given by (13) with $\tilde{K}_\phi^*(k) = 0$. In real-space representation, $G_{\phi\phi}^0(r)$ exhibits exponentialy damped oscillatory behavior [16],
\[ rG_{\phi\phi}^0(r) = -A_{\phi\phi} \sin(\alpha_r r + \theta) e^{-\alpha_0 r}, \] (19)
for $S_\lambda < T^*/\rho_0 < S_K$, where $T^*/\rho_0 = S_K$ and $T^*/\rho_0 = S_\lambda$ correspond to the Kirkwood and the $\lambda$-line respectively. For $T^*/\rho_0 > S_K$, a monotonic decay of correlations occurs. The larger one of the two decay lengths approaches the Debye length for $T^*/\rho_0 \to \infty$. For $T^*/\rho_0 < S_\lambda$, the correlation length is infinite, i.e. a charge-ordered phase with an oscillatory charge density is found in this approximation. The inverse decay length and the wave number of oscillations, $\alpha_0$ and $\alpha_1$, are given in Ref.[16].

When $\beta \Delta \Omega_{ho}[\phi, \eta]$ is taken into account in (17), then the correlation function defined in (17) differs from $G_{\phi\phi}^0$. In order to obtain a better approximation for $G_{\phi\phi}$, we first note that in the RPM, the dependence on $\eta(\mathbf{r})$ is strictly local. Thus, $\Delta \Omega$ can be easily minimized
with respect to $\eta(r)$ for each $\phi(r)$. As a result, we obtain

$$\eta(\phi(r)) = \sum_{n=1}^{\infty} \frac{a_n}{n!} \phi(r)^{2n},$$

where $a_n$ are functions of $\rho_0$ [17, 21]. In Ref. [17] the expansion in (20) was truncated at $n = 2$. From (20) and (11)-(15) we obtain the following approximation for the excess grand potential

$$\beta \Delta \Omega[\phi] = \frac{1}{2} \int \frac{d^d \phi}{(2\pi)^d} \tilde{G}_{\phi\phi}(k) \tilde{\phi}(k) \tilde{\phi}(-k) + \frac{A_4}{4!} \int dr \phi^4(r) + \frac{A_6}{6!} \int dr \phi^6(r) + O(\phi^8),$$

where $A_4$ and $A_6$ are combinations of $\gamma_{2m,n}$ (i.e. depend on $\rho_0$) and their explicit forms for the CS approximation for $f_h$ are given in Ref. [21].

In Ref. [17] $\tilde{G}_{\phi\phi}(k)$ was calculated in the self-consistent one-loop approximation. In this approximation, the $k$-dependence of $\tilde{G}_{\phi\phi}(k)$ is the same as the $k$-dependence of $\tilde{G}_{\phi\phi}^0(k)$, and

$$\tilde{G}_{\phi\phi}^{-1}(k) = \tilde{C}_{\phi\phi}(k) = c_0 + \beta^* \tilde{V}^*(k),$$

where

$$c_0 = \rho_0^{-1} + \left( \frac{A_4 G(c_0)}{2} + \frac{A_6 G(c_0)^2}{8} \right),$$

and the fluctuation-induced correction depends on

$$\mathcal{G}(c_0) \equiv \langle \phi(r)^2 \rangle = \int \frac{d^d \phi}{(2\pi)^d} \tilde{G}_{\phi\phi}(k).$$

The integral in (24) diverges because of the integrand behavior for $k \to \infty$. However, the contribution from $k \to \infty$ is unphysical (overlapping hard cores). When the fluctuations with $k \approx k_b$ dominate, which is the case for $T^*/\rho_0 \ll S_0 \approx 2.6$ [17], then the dominant contribution to the cutoff-regularized integral in (24) comes from $k \approx k_b$ and is cutoff-independent. In this case $\mathcal{G}(c_0) \propto 1/\sqrt{c_0}$ [17, 22]. The self-consistent solution of (22)-(24) gives $c_0$ that depends on the thermodynamic state in a rather nontrivial way [17], and leads to $\tilde{C}_{\phi\phi}(k_b) > 0$ for $T > 0$, i.e. the instability with respect to periodic ordering, $\tilde{C}_{\phi\phi}(k_b) = 0$, is shifted down to $T = 0$.

### III. EULER-LAGRANGE EQUATION FOR A CONFINED SYSTEM

In the previous section we considered the excess grand potential associated with local deviations of the charge- and number density of ions from the equilibrium values. In confinement, the inhomogeneities are induced by the presence of the boundaries. The difference
between the grand potential in a presence of the boundary and the grand potential of the same system in the bulk, $\Delta \Omega$, consists of two terms:

$$
\Delta \Omega = \Delta \Omega_b + \Delta \Omega_s.
$$

The first term in (25) is proportional to the system volume and is associated with the presence of inhomogeneities. This contribution was considered in the previous section. The second term contains the contribution to the grand potential associated with the fact that the fluid beyond the system boundary is replaced by the solid wall, and the interactions with the fluid particles are replaced by the interactions with the particles of the wall.

We assume that in the case of the RPM, $\Delta \Omega_b$ can be approximated by the expressions developed in sec.2. Moreover, we limit ourselves to small surface charge density that leads to small $\phi(r)$. In such a case terms of order $\phi^4$ can be neglected compared to terms of order $\phi^2$ in (21). Consistent with the assumption of small surface charge, we neglect the second and the third term in Eq.(21). However, for the second functional derivative of $\Delta \Omega_b$ we assume the function (22), and obtain the approximation

$$
\beta \Delta \Omega_b[\phi] \approx \frac{1}{2} \int d\mathbf{k} \tilde{\phi}(\mathbf{k}) \left( c_0 + \beta^* \widetilde{V}^*(\mathbf{k}) \right) \tilde{\phi}(-\mathbf{k}).
$$

(26)

By replacing $1/\rho_0$ by $c_0$ (compare (13) and (22)), we approximately take into account the effect of fluctuations. In Ref.[17], it was shown that for large values of $T^*/\rho_0$, the parameter $c_0$ differs from $1/\rho_0$ rather weakly. For small values of $T^*/\rho_0$, however, $c_0$ is significantly different from $1/\rho_0$, and the artifact of the MF approximation - namely the continuous transition to the charge-ordered phase present in MF and absent in reality, is replaced by the first order transition to an ionic crystal. The latter transition occurs for much higher density of ions [17,21]. Here we treat $c_0$ as a parameter depending on the thermodynamic state, such that

$$
R^* \equiv T^* c_0 + \widetilde{V}^*(k_b) > 0.
$$

(27)

$R^* \to 0$ for $T^* \to 0$, and increases for increasing $T^*$ and/or decreasing $\rho_0$. In this approximation $\tilde{G}_{\phi\phi}(k)$ depends on the thermodynamic state through the single parameter $R^*$. Precise dependence of $R^*$ on the thermodynamic state is not of primary importance in our study; we only need to ensure that the system is in the liquid phase. In Ref.[17] it was found at the same level of approximation as in the present study that at the liquid-solid coexistence
\( R^* \approx 0.2 \) for \( 0.25 < \rho_0 < 0.8 \). We shall thus assume that for RTILs and RTILs mixtures with neutral solvents the relevant values of \( R^* \) are \( 0.2 < R^* < 0.5 \).

To determine \( \phi(\mathbf{r}) \) corresponding to the minimum of \( \Delta \Omega \), we shall first transform the approximate expression for \( \Delta \Omega_b \) (Eq.(26)) to a more convenient form. Our aim is to develop an expression for \( \Delta \Omega_b \) in terms of a single integral in the real-space representation. From the minimum condition for such a functional one can obtain the Euler-Lagrange (EL) equation for \( \phi(\mathbf{r}) \) that can be solved easily.

Because of the long-range of the Coulomb potential, \( \tilde{V}^*(k) \) diverges for \( k \to 0 \), and cannot be expanded in a Taylor series. We note, however that the main contribution to the electrostatic energy comes from the charge-density waves, with the wavelength \( 2\pi/k_b \) corresponding to the minimum of \( \tilde{V}^*(k) \) at \( k = k_b \). Taking into account that \( \tilde{V}^*(k) \) is an even function of \( k \) (see (7)), we can consider a function of \( k^2 \), and expand it about the minimum at \( k^2 = k_b^2 \),

\[
\tilde{v}^*(k^2) \equiv \tilde{V}^*(k) = \tilde{V}^*(k_b) + \sum_{n=2}^{\infty} \frac{v^{(n)}}{n!} (k^2 - k_b^2)^n, \tag{28}
\]

where \( v^{(n)} \) denotes the \( n \)-th derivative of \( \tilde{v}^*(k^2) \) with respect to \( k^2 \) at \( k^2 = k_b^2 \). Using (28) and the equality

\[
\int \frac{dk}{(2\pi)^d} k^2 \tilde{\phi}(k) \tilde{\phi}(-k) = - \int d\mathbf{r} \phi(\mathbf{r}) \nabla^2 \phi(\mathbf{r}), \tag{29}
\]

where \( \nabla^2 \) denotes the Laplacian, we can write (26) in the form

\[
\beta \Delta \Omega_b[\phi] = \frac{\beta^*}{2} \int d\mathbf{r} \left[ R^* \phi(\mathbf{r})^2 + \phi(\mathbf{r}) \sum_{n=2}^{\infty} \frac{v^{(n)}}{n!} (-\nabla^2 - k_b^2)^n \phi(\mathbf{r}) \right]. \tag{30}
\]

It is instructive to consider (30) with the expansion truncated at the lowest-order term, and perform integration by parts. Neglecting the surface terms, we obtain

\[
\beta \Delta \Omega_b[\phi] = \int d\mathbf{r} \left[ A_0 \phi(\mathbf{r})^2 - A_2 \left( \nabla \phi(\mathbf{r}) \right)^2 + A_4 \left( \nabla^2 \phi(\mathbf{r}) \right)^2 \right] + \ldots \tag{31}
\]

where the coefficients

\[
A_0 = \frac{\beta^*}{2} \left( R^* + \frac{\partial^2}{2} k_b^4 \right), \tag{32}
\]

\[
A_2 = \frac{\beta^* v^{(2)} k_b^2}{2} \tag{33}
\]

and

\[
A_4 = \frac{\beta^* v^{(2)}}{4} \tag{34}
\]
are all positive. Note that the inhomogeneities \((\nabla \phi(\mathbf{r}) \neq 0)\) are favoured by the second term in (31). The functional (31) has the form first proposed by Brazovskii \[22\] for description of systems with mesoscopic inhomogeneities. We should note, however that in (31) the first term is given by a particularly simple expression, whereas in general the term describing the local dependence on the order parameter (OP) is given by a function \(f(\phi(\mathbf{r}))\) that may have different forms in different inhomogeneous systems. The Landau-Brazovskii (LB) functional was used or developed for description of block copolymers, microemulsion, systems with short range attraction and long-range repulsion (SALR), thin magnetic films with competing ferromagnetic and dipolar interactions, and even critical mixture with antagonistic salt \[24–28\].

For a semiinfinite system with the planar confining surface at \(z = 0\) (in the coordinate frame where \(\mathbf{r} = (x, y, z)\)), the EL equation for (31) takes the very simple form

\[
A_4 \frac{d^4 \Phi(z)}{dz^4} + A_2 \frac{d^2 \Phi(z)}{dz^2} + A_0 \Phi(z) = 0,
\]

where

\[
\Phi(z) = \int dx \int dy \phi(x, y, z)/A_S.
\]

In the above definition of the average charge at the distance \(z\) from the wall, the integration is over the surface in the \((x, y)\) plane with the area \(A_S \to \infty\).

The solution of (35) is a linear combination of four terms of the type \(\exp(\lambda z)\), with \(\lambda\) satisfying the equation

\[
A_4 \lambda^4 + A_2 \lambda^2 + A_0 = 0.
\]

The solutions are

\[
\lambda = \pm \alpha_0 \pm i\alpha_1,
\]

where

\[
\alpha_0 = k_b \left[ \frac{\sqrt{A} - 1}{2} \right]^{1/2}
\]

\[
\alpha_1 = k_b \left[ \frac{\sqrt{A} + 1}{2} \right]^{1/2}
\]

\[
A = 1 + \frac{4R^*}{|V^*(k_b)|(1 + k_b^2/2)}.
\]

In the semiinfinite system \(\Phi(z) \to 0\) for \(z \to \infty\), and

\[
\Phi(z) = \mathcal{A} e^{-\alpha_0 z} \sin(\alpha_1 z + \theta),
\]
FIG. 1: The inverse decay length $\alpha_0$ (left), and the wavenumber $\alpha_1$ (right) as functions of $R^* = T^*c_0 + \tilde{V}(k_b)$. $R^*$ is an increasing function of the dimensionless temperature $T^*$ and a decreasing function of the dimensionless number density $\rho_0$. Dashed lines represent Eqs. (39) and (40). Solid lines represent the corresponding inverse lengths in the expression for the correlation function obtained in Ref. [16].

where the amplitude $A$ and the phase $\theta$ should be determined from the boundary conditions. The latter should follow from the surface contributions to $\Delta \Omega$.

When we apply the continuous description to the structure at the molecular scale, we face some ambiguities, or dependence on the definitions, leading to problems with finding a unique expression for the second term in (25). In particular, it is necessary to assume where the system boundary ($z = 0$) and the surface charges are precisely located. Here we assume that the charge is uniformly distributed over the core of the particle. In order to precisely define $\Phi(z_0)$, we consider the slab parallel to the wall, $z \in [z_0 - 1/2, z_0 + 1/2]$ (recall that length is in $\sigma$-units). We assume that $\frac{\pi}{6} \Phi(z)$ denotes the fraction of the volume of this slab that is occupied by the cations minus the fraction of the volume of this slab that is occupied by the anions.

We choose simulations of Ref. [11] for comparison with predictions of our theory, because these simulations concern the RPM, i.e. the model to which the current version of our theory is restricted. In order to compare our results with the results of the simulations in Ref. [11], we assume that the system boundary consists of homogeneously charged spheres, with the centers homogeneously distributed at the $z = 0$ plane. The total charge of these fixed spheres per area of the $z = 0$ plane is equal to $\sigma_0$. Including this fixed charge in the charge profile $\Phi(z)$, we obtain the condition $\Phi(0) = \sigma_0$. Moreover, we require the electroneutrality
FIG. 2: Cartoon illustrating $\Phi(z)$ in this continuous theory applied to the microscopic length-scale. $\frac{\pi}{6} \Phi(z)$ is the fraction of the volume of the slab between the dashed lines at $z - \sigma/2$ and $z + \sigma/2$ that is occupied by the cations (plus sign) minus the fraction of the volume of the slab that is occupied by the anions (minus sign). The system boundary consists of negatively charged hard spheres with the centers fixed at the $z = 0$ plane. We include the charge of the boundary layer in $\Phi$, hence $\Phi(0) = \sigma_0$, where $e\sigma_0$ is the total charge of the surface layer divided by the area $A_S$ of the $z = 0$-plane.

of the whole system, $\int_0^\infty dz \Phi(z) = 0$. From the two above conditions we obtain

$$A = \frac{\sigma_0}{\sin \theta}, \quad \theta = \arctan \left( -\frac{\alpha_1}{\alpha_0} \right).$$

(43)

Two examples of the charge-density profile are shown in Fig. 3. We choose small surface charges, since the approximate theory is valid only for small $\Phi$.

From the charge profile we can obtain the electrostatic potential $\Psi(z)$, using the Poisson equation. For our geometry and for $\Psi(z) \to 0$ for $z \to \infty$, we can write the Poisson equation in the form (recall that $\Phi$ and $z$ are dimensionless)

$$\Psi(z) = \frac{4\pi e}{\varepsilon \sigma} \int_z^\infty dz' (z - z') \Phi(z').$$

(44)

The explicit expression can be easily obtained from (41), (42) and (43),

$$\Psi(z) = \frac{4\pi e \sigma_0}{\varepsilon \sigma \sin \theta (\alpha_0^2 + \alpha_1^2)} \left[ \left( \frac{\alpha_1^2}{\alpha_0^2} - \frac{\alpha_0^2}{\alpha_1^2} \right) \sin(\alpha_1 z + \theta) - 2\alpha_0 \alpha_1 \cos(\alpha_1 z + \theta) \right] e^{-\alpha_0 z}.$$  

(45)

In Fig. 4 we plot $U(z) = \Psi(z) e/k_B T$ for ions with $\sigma = 1nm$, $\epsilon = 1$, and surface charge density $\sigma_0 \approx 0.8\mu C/cm^2$ and $\sigma_0 \approx 8\mu C/cm^2$, in order to compare the order of magnitude of our result with the simulations performed in Ref. [11].
FIG. 3: The charge-density profile $\Phi(z)$ (42 and 43) (in $e\sigma^{-3}$-units), for $R^* = 0.25$. The surface charge density (in $e\sigma^{-2}$-units) is $\sigma_0 = -0.05$ (solid line) and $\sigma_0 = -0.5$ (dashed line). Distance is in units of the ion diameter $\sigma$. When $\sigma = 1nm$, the two values of the surface charge density correspond to $\sigma_0 \approx 0.8\mu C/cm^2$ and $\sigma_0 \approx 8\mu C/cm^2$ respectively, the case studied in simulation in Ref.[11].

We did not try to precisely adjust the thermodynamic state to the thermodynamic state in the simulations. Instead, we compared the charge and potential profiles for different values of $R^*$ within the stability region of the liquid phase (Fig.5). For $R^* \leq 0.5$, the potential has the shape very similar to the shape obtained in simulations already in the simplest version of our theory. The decay length decreases with increasing $R^*$, (see Fig.1), but for the relevant value of $R^*$, $0.2 < R^* < 0.5$, we see essentially the same number of peaks as in the simulations. Moreover, the order of magnitude for the rescaled potential is in very good agreement with the simulation results. We cannot expect quantitative agreement in such a simplified theory. Moreover, in contrast to the simulations, we did not take into account the polarization effects of the ions.

The approximation for $\Delta \Omega$ can be improved when more terms are taken into account in the expansion in Eq.(30). When $N$ terms in Eq.(30) are taken into account, then the EL equation is

$$R^* \phi(r) + \sum_{n=2}^{N} \frac{v(n)}{n!} (-\nabla^2 - k^2_0)^n \phi(r) = 0.$$  (46)

The solution has the exponential form $\exp(\lambda z)$, where $\lambda$ satisfies the above equation with $\nabla^2$ replaced by $\lambda^2$. Note, however that the series in (30) converges (see (28)), and we can
FIG. 4: The re-scaled electrostatic potential $U = \Psi(z)e/k_BT$ (dimensionless), for $R^* = 0.25$, $\epsilon = 1$ and $T = 300K$. The surface charge density (in $e\sigma^{-2}$-units) is $\sigma_0 = -0.05$ (solid line) and $\sigma_0 = -0.5$ (dashed line). Distance is in units of the ion diameter $\sigma$. When $\sigma = 1nm$, the two values of the surface charge density correspond to $\sigma_0 \approx 0.8 \mu C/cm^2$ and $\sigma_0 \approx 8 \mu C/cm^2$ respectively, the case studied in simulations in Ref.\[11\].

FIG. 5: The rescaled electrostatic potential $U = \Psi(z)e/k_BT$ (dimensionless) for the surface charge density $\sigma_0 = -0.5$ (in $e\sigma^{-2}$-units), $\epsilon = 1$ and $T = 300K$. When $\sigma = 1nm$, the surface charge density corresponds to $\sigma_0 \approx 8 \mu C/cm^2$. Solid and dashed lines correspond to $R^* = 0.22$ and $R^* = 0.5$ respectively. Distance is in units of the ion diameter $\sigma$.

obtain $\lambda^2$ by solving

$$\tilde{C}_{\phi\phi}(k) = c_0 + \beta^* \tilde{v}(k^2) = 0,$$

with $k^2$ replaced by $-\lambda^2$. The zeros of the above function were determined in Ref.\[16\], and
we compare the so obtained $\alpha_0$ and $\alpha_1$ with the result of our simple approximation (39)-(40) in Fig.1.

While our simple approximation (39) rather well reproduces $\alpha_0$ for $R^* < 5$, $\alpha_1$ given by (40) is more and more overestimated for increasing $R^*$. In the region of interest in ionic liquids ($0.2 \leq R^* < 0.5$), however, the simple approximation is quite reasonable; for $R^* \leq 0.5$ the relative deviation is $\leq 9\%$. The charge-density profile obtained by minimization of the functional (30) is only slightly different from the profile shown in Fig.3 and obtained by the minimization of the simple approximation (31).

The accuracy of the approximate EL (35) is directly linked with the accuracy of the correlation function (22) with $\tilde{V}^*(k)$ approximated by the expansion (28) truncated at $n = 2$. For $2 < k < 3$ the accuracy of the approximate form of the correlation function increases when $R^*$ decreases to small values, consistent with the result for $\alpha_0, \alpha_1$. The very simple approximation is thus reasonable for both the correlation function and the structure near the wall for the thermodynamic states relevant for ionic liquids.

![FIG. 6: The correlation function for $R^* = 0.25$ with $\tilde{V}^*(k)$ given by (7) (solid line) and by the expansion (28) truncated at $n = 2$ (dashed line).]
IV. SUMMARY AND CONCLUSIONS

The aim of this work was a development of a simple theory for the structure of the ionic liquid or ionic liquid mixture with a neutral solvent, near a charged boundary. The theory is based on the mesoscopic theory for ionic systems developed for the bulk in Refs. [15–20]. Even though our theory is essentially of the MF character, we still obtain oscillatory decay of the charge density for increasing distance from the charged surface. For the entropy part of the grand potential we have made the local density approximation, therefore packing effects of hard spheres are not taken into account through this contribution to the grand potential. We have not included, however, the contributions to the electrostatic energy associated with overlapping cores of the ions. We take into account that only pairs of ions separated by distances larger than the sum of their radii contribute to the internal energy simply by assuming that the pair distribution function in the expression for the internal energy vanishes for shorter distances. By not including the electrostatic energy of overlapping cores, we set the distance between the anion and the cation that corresponds to the minimum of the energy. This is the origin of the oscillatory decay of the charge density on the length scale set by the size of the ions.

Our results for the charge profile and for the electrostatic potential have been obtained from the EL equations for the excess grand potential approximated by the functional of the second order in the local charge density $\phi$ (see Eq. (26)). In addition, we took into account fluctuations by renormalization of the parameter depending on the thermodynamic state in this functional. However, in MF the functional has precisely the same form, and leads to the same shape of the charge density profile, except that for overestimated values of $T^*/\rho_0$.

We conclude that it is not the MF approximation that leads to the monotonic decay of the charge density and the potential near the charged surface, but the specific version of MF, with point-like charges. Neglecting the finite size of ions is justified at very low densities, but not in IL. The key factor leading to the oscillatory decay of the potential is the presence of the impenetrable cores. In the DFT theories the sophisticated form of the entropy of the hard spheres leads to the oscillatory profile [13]. In our theory, it is sufficient to take into account the finite size of the ions only in the expression for the internal energy.

We have made other simplifying assumptions in addition to the local density approximation to obtain a simple analytic expression for the charge density. Because of that, we
cannot expect quantitative agreement of our predictions with exact or simulation results. Still, the agreement with simulations for the RPM is surprisingly good. The very simple analytical expressions for the charge and potential profiles is a clear advantage of the theory. Moreover, the theory can be extended in many ways. We can include SR interactions, or consider ions of different sizes, as done in the bulk in Ref.\cite{20,29}, and include higher order terms in (21) in the case of larger surface charge.

In Ref.\cite{30}, co-authored by Lesser Blum, the first sentence in the introduction reads: “Analytical theories of ionic solutions are of practical interest, since the properties of real systems can be represented in terms of (hopefully) relatively simple equations.” We hope that the present work is in the same spirit. The properties of real systems are represented in terms of very simple equations (42) and (45).

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