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If bulk properties of simple molten salts may be reasonably well understood in terms of the primitive model, the situation with respect to surface properties is less satisfactory. It has been shown that a simple model for the distributions at the free surface of a molten salt can give surface tension and surface energy in reasonable accord with experiment, provided that a factor guaranteeing local electroneutrality is introduced. In this model, properties are given in terms of bulk-salt distribution functions, for which the primitive model is used. The present work extends this model to the electrocapillary curve, i.e., variation of surface tension with surface charge density. The calculations are like those for the free surface, corresponding to the point of zero charge. The local electroneutrality correction, while extremely important for the magnitude of the surface tension, is much less important for its variation with surface charge, and hence the electrical capacitance. Our capacitances, derived from surface charges and potential drops derived from our model, are much too small, whereas the Gouy–Chapman model gives values which are much too large. The calculated variations of surface tension and potential drop with surface charge do not satisfy the thermodynamically derived Lippmann equations; neither does one obtain the same surface tension from different thermodynamically equivalent formulas. In order to understand the reasons and to improve the situation, we show how thermodynamic consistency may be restored to our model. Capacitances are still numerically much smaller than those reported experimentally.

I. Introduction

Molten salts are important in batteries and other technological applications, but are also of great theoretical interest. They constitute the simplest electrolytes, involving only two charged species, with no uncharged species (e.g., the solvent in an electrolytic solution), and with both species describable by classical mechanics (unlike the conduction electrons of metals). Although the precise form of the forces between ions, whether they can be assumed pairwise additive,[1] and whether one needs to introduce a dielectric constant to represent their polarizability, is not completely settled, it is clear that treatment of the Coulombic attractions and repulsions constitutes a major part of the theoretical description of these systems. Indeed, many bulk properties of the molten salts can be understood in terms of the primitive model, which considers the ions as charged hard spheres in a dielectric medium.[2-8]

Understanding of surface properties is less advanced than understanding of bulk properties, although surface properties are of primary importance in electrochemistry. One of the basic concepts of modern electrochemistry[9-12] is the polarizable electrode, a charged interface in which a change in surface charge density is accompanied by changes in the surface tension and in the potential drop across the interface, but not by current flow, so that it behaves like a capacitor. Such a system is usually exemplified by mercury in aqueous solution, but can be realized also by a metal in a molten salt.[13-15] The Lippmann equation[9,11,16-17] relates the variation of surface tension with potential drop (electrocapillary curve) to the surface charge. The surface tension can be measured directly and also the derivative of surface charge with potential drop, which is the capacitance (although the meaning of some of the measurements has been criticized[15]). Measured properties are actually those of the interface as a whole, but conventional electrochemical wisdom is that the metal's contribution to certain properties is unimportant.[18] For example, if one distinguishes between charged components of the salt and those of the metal, one shows[11] that the potential drop consists of salt and metal contributions (which are not necessarily the same as for free salt and metal surfaces), so that, if the metal's capacity is large, the capacity of the interface is essentially that of the salt. (This is emphatically not the case for the surface tension of the interface, which is dominated by that of the metal.)

A number of approaches to learning about the polarizable molten salt–metal interface are being taken. Monte Carlo and molecular dynamics simulations for the liquid–vapor interface of molten salts have been performed, giving information on the ionic distribution functions near the surface.[19] These calculations have recently been extended[20] to the interface at a charged repulsive wall (electrode) with surface tension and capacitance being calculated. Various statistical mechanical approaches are possible but have so far usually been tried in the electrolyte, rather than the molten salt, regime of the interface. The density profile, as well as the two-particle distribution functions

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needed for a calculation of surface tension, can be expressed in terms of the direct correlation functions c_{ij} of the interface, and the short-range character of the c_{ij} suggests that a reasonable approximation is to replace them by the corresponding functions for the bulk. This has been done[21-25] by using a variety of approximations for the bulk functions, coupled with various approximations to the integral equation determining the wall-particle correlation functions (density profiles). Tests have been for the primitive model; indeed one flaw of this model, the replacement of the solvent by a continuous dielectric, becomes very important when the model is applied to the molten salt interface, since the dielectric constant cannot be separated from the ion density profile. The extension of density functional theories to systems involving Coulombic interactions[26-28] has also led to calculations of some properties of the liquid–vapor interface for molten salts.[29,30] By use of a number of approximations for the response functions in the surface, these theories give expressions which allow the use of properties of the bulk to calculate properties of the surface. Our own work[31-34] has involved generating approximate distribution functions for the surface from those for the bulk and calculating surface tensions and surface energies for the free surface.

It is this approach that we extend, in the present paper, to calculation of the electrocapillary curve (surface tension as a function of surface charge) of the salt part of the interface. At the potential of zero charge (pzc), the model for the salt (in contact with a metal electrode) is identical with that for the salt in contact with its vapor (free surface). This is possible if the ion density profiles are so sharp that the repulsion due to the metal does not change their shape much. Some workers[14,35] have argued, on the basis of electrocapillary measurements, that the alkali halide surface in the electrode is not much changed, relative to the free surface, by the metal at the pzc. At potentials other than the pzc, it is difficult to perform calculations for the salt alone, since it carries a net charge. Thus the metal in the interface is represented in our calculations by a charged plane and calculated results for the globally neutral interface are compared to the corresponding properties for an ideal capacitor, formed from two charged planes. We will require knowledge of the bulk correlation functions of the salt, which are obtained from the generalized mean spherical approximation for equal sized charged hard spheres.[8,36] The simpler mean spherical approximation, which has been extended to unequal ion sizes,[7,37,38] has serious deficiencies in the pair distribution functions.[8,37,39,40] Thus the salt is being considered in the context of the restricted primitive model. The dielectric constant is taken as unity, which is consistent[7] with rigid ions; for a surface problem, there are difficulties, related to treatment of image forces, attached to using a value other than unity.[31,41] Problems arising from the assumptions about the bulk salt, and from other aspects of the model, are discussed in section VII.

Section II presents our model for the surface and the formulas used for calculation of the surface tension of the charged interface. The Fowler model for the distribution functions, and our modification of it for charged-particle systems, are presented. The essence of the modification is satisfaction of a constraint of local electroneutrality; the method for accomlishing this is discussed in section III, and results for the variational calculations of the "electroneutrality functions" are presented. The calculation of surface tensions is carried out in section IV. In section V, the results are presented, and the Lippmann equation is discussed.

One aim of statistical mechanical calculations like the present one must be to make connection with the thermodynamic description, which defines surface properties in a way different from ours; the thermodynamic definitions do not deal with the actual physical description of surface charges, etc. On the other hand, internal consistency is built in, whereas statistical mechanically calculated quantities do not necessarily satisfy thermodynamic relations, which become a test of the consistency of our assumptions. The Lippmann equation is one of these thermodynamic relations; as shown in section V, we find it not to be verified. A discussion points out a problem with the Born–Green–Yvon equilibrium condition, which leads to other surface tension formulas and redefined density profiles. None of our models give capacitances in accord with experiment. Section VI considers other ways in which the model may be improved and directions for future work.

II. Calculation of Surface Properties

The Kirkwood–Buff formula[42] gives the surface tension in terms of the interparticle forces and the two-particle distributions $\rho_{ij}^{(2)}$, where $\rho_{ij}^{(2)}(\vec{r}_1, \vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2$ gives the number of pairs of particles such that a particle of species i is in the volume element $d\vec{r}_1$ at $\vec{r}_1$ and a particle of species j is in $d\vec{r}_2$ at $\vec{r}_2$. It is assumed that only pairwise interactions are present. We write

$$\rho_{ij}^{(2)} = \rho_i^{(1)}(z_1)\rho_j^{(1)}(z_2)g_{ij}(\vec{r}_1,\vec{r}_2) \qquad (1)$$

where $\rho_i^{(1)}$ is the one-particle density (density profile) of species i, depending only on the coordinate perpendicular to the interface, and the correlation function g_{ij} depends on $\vec{r}_1$ and $\vec{r}_2$ in the interface. In the bulk, $\rho_i^{(1)}$ is, of course, a constant and g_{ij} can depend only on the interparticle distance r_{12}. The Fowler approximation[42-44] replaces the g_{ij} in (1) by the corresponding bulk functions so that, given the profiles, insertion of (1) into the Kirkwood–Buff formula allows the calculation of the surface tension in terms of the properties of the bulk fluid. (Modern theories of

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the interface make the same replacement for the direct correlation function[45] which seems more reasonable because of the shorter range of this function.) While reasonable results can be obtained for some fluids by this procedure, molten salts are emphatically not among them.[31] The problem seems to be due to the Coulombic interactions, which impose[46] a local electroneutrality condition on the correlation functions.

The local electroneutrality condition is that the net charge around an ion should be equal and opposite to the ion's charge. (It is not implied that the net charge density be zero everywhere; other authors have referred to this as "local electroneutrality".) This is not obeyed by the Fowler approximation because the surface, as expressed by the factor $\rho_i(z)$ in (1), truncates the two-particle distribution.[47] We have discussed[32,34] modification of the Fowler approximation to guarantee local electroneutrality. Great improvements in surface tension and surface energy for the free (electrically neutral) surface of a molten salt have been obtained on introducing this modification.[31-34] Croxton and McQuarrie[48] found imposition of a similar condition on their closure of the Born–Yvon–Green (BYG) equation for charged spheres at a charged surface led to improved results and suggested a similar modification should ameliorate theories which use bulk c_{ij} for the surface. Local electroneutrality was also used[49] in a theory for getting (bulk) g_{ij} of charged hard spheres in terms of g_{ij} for neutral spheres. In the present work, we extend the electroneutrality formulas to the salt surface in the presence of an external field. In this case, a separation of positive and negative charges in the salt leads to a double layer and a potential drop across the surface region. As for the free surface, our model yields a formula for surface tension which involves integrals over the bulk distribution functions; the function introduced to guarantee local electroneutrality is also determined by properties of the bulk distribution function (section III).

Our bulk salt is described by the restricted primitive model: anions and cations are oppositely charged hard spheres of equal size with the dielectric constant taken as unity. The distribution functions for the bulk are calculated according to the generalized mean spherical approximation (GMSA).[36] Although the simpler mean spherical approximation (MSA) seems to give reasonable values for thermodynamic properties[3,39] and although the MSA has been solved[6] for hard spheres of different sizes we do not use it here because it does not describe well the detailed shapes[6,36,37,39] of the g_{ij} which are central to our calculations. We note that other extensions of the MSA for the primitive model have been proposed and studied.[50-54] While first developed and tested for electrolyte solutions, the GMSA seems to work better[8,53] for higher concentrations and thus for molten salts (with dielectric constant unity).

As for the assumption of equal sizes for cation and anion cores, it seems not to be a bad one for bulk properties even

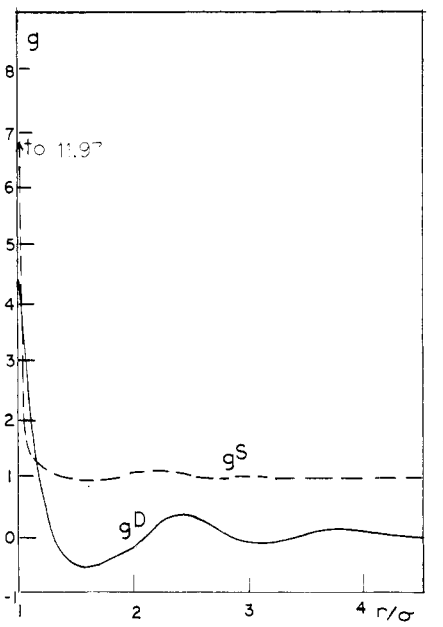

Figure 1. Calculated two-particle bulk distribution functions from the generalized mean sphrical approximation. σ is the hard-sphere diameter. g^S and g^D are defined in eq 2 and 3.

if the ions are actually of different sizes because, except where the disparity in ion sizes is very large (Li salts), ions of opposite charge are much more likely to approach to small distances than like-charged ions.[3-5,55-60] The core size parameter we use in our calculations is in fact roughly appropriate for NaCl.[5,6,32,33] However, the difference in ion sizes must be important in determining the structure of the surface, since this difference should produce a double layer and potential drop even for the free surface or for the interface at the potential of zero charge. The larger ions (usually the anions) will tend to protrude from the free surface, forming a layer of charge, and the absence of electric fields in the bulk implies an oppositely charged layer must exist below it. For ions against a hard wall (the metal of the electrode) the reverse should obtain. Sluckin[30] has recently discussed this effect using a perturbation theory applied to a treatment of these systems by the density functional formalism.[28,29] Since our model assumes identical density profiles for cations and anions in the absence of an external field, it seems most reasonable to say we are describing a fictitious salt for which anions and cations both have a hard-sphere diameter of 2.55 Å, representing the averaging of anion and cation diameters for NaCl.

The radial distribution functions for a bulk liquid whose particles interact by Coulomb plus hard-sphere potentials are calculated according to the generalized mean spherical approximation (GMSA) with the formulas of Stell and co-workers[3,36,52] which generate g^D and g^S where

$$g^D(r) = \tfrac{1}{2}[g^b_{+-}(r) - g^b_{++}(r)] \quad (2)$$

$$g^S(r) = \tfrac{1}{2}[g^b_{+-}(r) + g^b_{++}(r)] \quad (3)$$

(superscript b refers to bulk). The distribution functions we obtained are given in Figure 1. In the absence of external field, i.e., at the potential of zero charge, the

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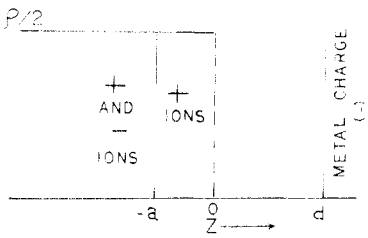

Figure 2. Ion and metal charge densities for use in two-particle distributions, eq 1.

expression for the surface tension does not involve g^S, so it was not calculated in our previous work. The local electroneutrality conditions will be imposed by modifying g^D, leaving g^S unchanged. Away from the potential of zero charge, where positive and negative ion distributions are different, g_{+-} can differ from g_{-+}, and g_{++} from g_{--}. The quantities $g_{+-} - g_{++}$ and $g_{-+} - g_{--}$ can thus be different in the surface region, and two functions will be determined to guarantee local electroneutrality. We write

$$g_{+-}(\vec{r}_1\vec{r}_2) + g_{++}(\vec{r}_1\vec{r}_2) = 2g^S(r_{12}) \quad (4a)$$

$$g_{-+}(\vec{r}_1\vec{r}_2) + g_{--}(\vec{r}_1\vec{r}_2) = 2g^S(r_{12}) \quad (4b)$$

$$g_{+-}(\vec{r}_1\vec{r}_2) - g_{++}(\vec{r}_1\vec{r}_2) = 2f_+\left(\frac{z_1 + z_2}{2}\right)g^D(r_{12}) \quad (5a)$$

$$g_{-+}(\vec{r}_1\vec{r}_2) - g_{--}(\vec{r}_1\vec{r}_2) = 2f_-\left(\frac{z_1 + z_2}{2}\right)g^D(r_{12}) \quad (5b)$$

and find f_+ and f_- from the electroneutrality conditions. The solution of the equations is discussed in the next section.

The one-particle densities remain to be specified in (1). The simplest assumption is to take them as stepfunctions as was done for some of our calculations of the free surface.[31-33] The abrupt decrease of the density to zero is more appropriate for a fluid near a repulsive wall than for a free surface (for which an attempt to consider other profiles was made[34]). It must be admitted that a condition exists on the contact density at a hard wall[61] which is not satisfied by the assumption of stepfunctions. Furthermore, a fluid of particles with repulsive cores should have an oscillating density profile at a wall and molecular dynamics calculations[28] for a molten salt show that the presence of Coulombic forces does not remove the oscillations (although charge ordering or layering seem to be absent, even for a charged wall). Of course, our $\rho_{ij}^{(2)}$ do not satisfy the BYG equations with stepfunctions for the $\rho_i^{(1)}$, and there is some ambiguity in the definition of surface tension when such an inconsistency is present.[62] Our use of stepfunction profiles for surface tension calculation is based on a hope that details of the profiles will average out (see section VI for generation of oscillatory profiles from the model).

The charge distribution is shown in Figure 2 which implies that the centers of the first layer of ions of the salt lie in the plane $z = 0$. The displacement a is determined by the charge density according to

$$a\rho e/2 = -q_M \quad (6)$$

which represents global electroneutrality, q_M being the charge per unit area on the "metal" and $\rho/2$ the density of anions or cations in bulk salt. The value of d, which determines the location of the metal's charge, should be related to the distance of closest approach between ions of the salt and the metal surface. If the ionic radius of the metal ions is R_M and the charge density q_M is supposed to lie on the first layer of ions, the estimate for d would be $R_M + {}^1/_2\sigma$, where σ is the ionic core diameter. Finally, we note that all properties should be unchanged by a change in the sign of all charges, so the electrocapillary curve is symmetric about the pzc.

III. Imposing Local Electroneutrality

The local electroneutrality condition is that the net charge surrounding a positive (negative) ion at z should be equal to one negative (positive) charge. This includes the charges on the metal as well as the charges of other ions in the salt. In terms of the one- and two-particle distributions, the condition for a positive ion is

$$e\int d\tau_2\,[\rho_{+}^{(2)}(\vec{r}_1\vec{r}_2) - \rho_{+-}^{(2)}(\vec{r}_1\vec{r}_2)]/\rho_{+}^{(1)}(z_1) + e\int d\tau_2\,\rho_d(\vec{r}_2) = -e \quad (7)$$

Here, the charge density of the metal is

$$\rho_d(\vec{r}_2) = q_M\delta(z_2 - d) \quad (8)$$

and of course is uncorrelated ($g = 1$) with the ions of the salt. On introduction of the assumptions of eq 4 and 5, eq 7 becomes

$$\int d\tau_2\left[(\rho_-(z_2) - \rho_+(z_2))g^S(r_{12}) + (\rho_-(z_2) + \rho_+(z_2))f_+\left(\frac{z_1 + z_2}{2}\right)g^D(r_{12}) - \rho_d(z_2)\right] = 1 \quad (9)$$

The corresponding equation for the charge around a negative ion is

$$\int d\tau_2\left[(\rho_+(z_2) - \rho_-(z_2))g^S(r_{12}) + (\rho_+(z_2) + \rho_-(z_2))f_-\left(\frac{z_1 + z_2}{2}\right)g^D(r_{12}) + \rho_d(z_2)\right] = 1 \quad (10)$$

where only values of $z_1 \leq -a$ are of interest. If $\rho_d = 0$ and ρ_+ and ρ_- are identical for the potential of zero charge, (10) becomes the same as (9) and g^S does not appear.

Equations 9 and 10 may be simplified by writing g^S as $1 + h^S$. The terms in 1 represent the total charge of the salt, which is equal and opposite to the total charge on the metal:

$$\int[\rho_+(z) - \rho_-(z)]\,dz = -g_M = -\int\rho_d(z)\,dz$$

Thus the term in ρ_d disappears and the local electroneutrality equations do not involve the metal charge distribution. Equation 9 may be written, when stepfunctions are inserted for the density profiles, as

$$2\pi\rho\int_{-\infty}^{\infty}dx\,[\theta(-2x + z_1) + \theta(-2x + z_1 - a)]f_+(z)G_D^{(1)}(2|x - z_1|) - 1 + \pi\rho\int_0^{\infty}r\,dr\,h^s(r)\int_{z_1-r}^{z_1+r}dz_2\,[\theta(-z_2 - a) - \theta(-z_2)] = 0 \quad (11)$$

We have introduced the abbreviation $G_D^{(1)}$ for the first moment of g^D. When z_1 is large and negative, the terms in h^S vanish in (11) because h^S is of limited range. The equation and that corresponding to (10) become

$$2\pi\rho\int_{-\infty}^{\infty}dx\;2f_{\pm}(x)G_D^{(1)}(2|x - z_1|) = 1 \quad (12)$$

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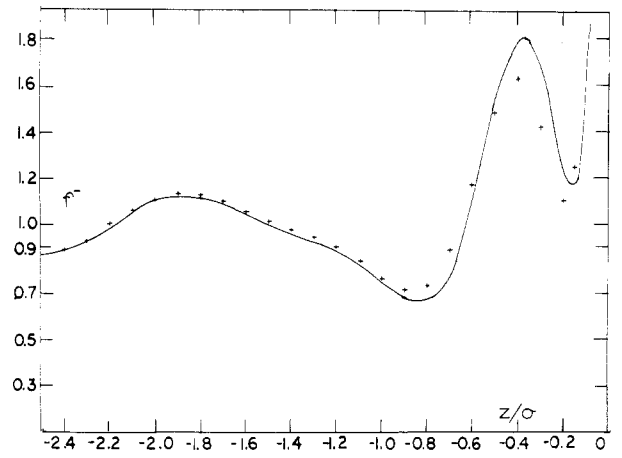

Figure 3. Calculated electroneutrality functions for $a = 0.1\sigma$. Solid curve is f^-, points + are f^+, which is generally close to f^-.

since the presence of $G_D^{(1)}$, which vanishes for large arguments, means only values of x which are large and negative contribute. Equation 12 is satisfied by $f_\pm(x) = 1$, because

$$\int_{-\infty}^{\infty} dx\ G^{(1)}(2|x - z_1|) = 2\int_0^{\infty} du \int_{2u}^{\infty} dr\ rg^D(r) = \int_0^{\infty} dr\ r^2 g^D(r) = (4\pi\rho)^{-1} \quad (13)$$

Therefore $f_\pm(z) \to 1$ as $z \to -\infty$.

The functions f_+ and f_- are determined variationally, by determining parameters in a trial function

$$f(z) = \sum_i C_i z^i e^{-\alpha_i(z-z_j)^2} + 1$$

so as to minimize the integrated square of the deviation from zero.[33] (A previous treatment (for uncharged surface) accomplished this[34] by representing the electroneutrality function f by a cubic in each of a large number of intervals.) The resulting functions are oscillatory, as might be expected, and generally all resemble each other. The terms dependent on the field, through a in (11), are in fact quite small. Some of these results are shown in Figure 3. We may note that our correlation functions (eq 1, 4, and 5) do not guarantee the symmetry

$$\rho_{+-}^{(2)}(\vec{r}_1,\vec{r}_2) = \rho_{-+}^{(2)}(\vec{r}_2\vec{r}_1)$$

between the two-particle distributions. The symmetry would require $g_{+-} = g^S + g_+^D$ to be identical with $g_{-+} = g^S + g_-^D$ and hence $f_+[(z_1 + z_2)/2]$ to equal $f_-[(z_1 + z_2)/2]$. Since in fact f_+ and f_- are only slightly different, the symmetry is effectively assured. An idea of how well one can satisfy the electroneutrality conditions is gained from the sum of the squares of the values of (11) or (12) evaluated for 100 values of z_1. It must be noted that there is always a doubt[63] whether a solution to an equation like (11) actually exists; in fact, the physics of the present situation mean that a mean-square solution, minimizing the mean-square deviation of the left side from zero, is what we actually should seek.

The calculations we perform in the present paper are for $a = 0.05\sigma$ and 0.10σ. The smaller value corresponds to a charge per unit area $|q_M|$ of 9634.3 esu/cm^2 or 3.2136 μC/cm^2.

(63) G. F. Miller, "Fredholm Equations of the First Kind", in "Numerical Solution of Integral Equations", L. M. Delves and J. Walsh, Ed., Clarendon, Oxford, 1974, p 195. C. T. H. Baker, "The Numerical Treatment of Integral Equations", Clarendon, Oxford, 1977, Chapter 5.

TABLE I: Contributions of Hard-Sphere Interaction to Surface Tension (dyn/cm)

$\bar{a}$	$\gamma_{HS}^{(1)}g^S(\sigma)$	$\gamma_{HS}^{(2)}g^D(\sigma)$	γ_{HS}
0.00	−306.43	0.00	−306.43
±0.05	−305.66	1.12	−304.54
±0.10	−303.38	4.74	−298.64

IV. Calculation of Surface Tension

The Kirkwood–Buff formula for the surface tension of a multicomponent fluid is

$$\gamma = \sum_{ij} \int dz_1 \int d\vec{r}_{12}\ \rho_{ij}^{(2)} u_{ij}'(r_{12})(x_{12}^2 - z_{12}^2)/2r_{12} \quad (14)$$

where i and j run over species and u_{ij} is the interaction potential between a particle of species i and a particle of species j, assumed to be a function of the interparticle separation only. We have three kinds of particles: positive ions, negative ions, and charges of the "metal" at d. There are no correlations between particles of the third kind and either of the first two, or between particles of the third kind; in such cases, we write $\rho_{ij}^{(2)}(\vec{r}_1\vec{r}_2) = \rho_i(z_1)\rho_j(z_2)$, whereas $\rho_{ij}^{(2)} = \rho_i(z_1)\rho_i(z_2)g_{ij}$ where correlations exist. The interaction potentials u_{ij} consist of the electrostatic interaction, which is present for all particles, and the hard-sphere repulsion, for particles of the molten salt only. Thus the surface tension has two parts

$$\gamma = \gamma_{HS} + \gamma_{EL} \quad (15)$$

corresponding to the two parts of u_{ij}.

The hard-sphere part, on introducing our assumptions for the g_{ij}, is, after a change of variables

$$\gamma_{HS} = -(\pi/2\beta)\int_{-\infty}^{\infty} dw \int_{-\sigma}^{\sigma} dv\ (\sigma^2 - 3w^2)\Big\{g^s(\sigma) \times \Big[\rho_+\Big(v - \frac{w}{2}\Big) + \rho_-\Big(v - \frac{w}{2}\Big)\Big]\Big[\rho_+\Big(v + \frac{w}{2}\Big) + \rho_-\Big(v + \frac{w}{2}\Big)\Big] + g^D(\sigma)\Big[f^+(v)\rho_+\Big(v - \frac{w}{2}\Big) - f^-(v)\rho_-\Big(v - \frac{w}{2}\Big)\Big] \times \Big[\rho_-\Big(v + \frac{w}{2}\Big) - \rho_+\Big(v + \frac{w}{2}\Big)\Big]\Big\} \equiv g^S(\sigma)\gamma_{HS}^{(1)} + g^D(\sigma)\gamma_{HS}^{(2)} \quad (16)$$

Here $\beta = 1/kT$, $v = {}^1/_2(z_1 + z_2)$, $w = z_2 - z_1$, and we are using the usual treatment[64] of the hard-sphere term, requiring an integration by parts in r_{12}. After some further algebra, we find

$$\gamma_{HS}^{(1)} = -\frac{\pi\rho^2}{4\beta}\Big(\frac{\sigma^4}{2} - \frac{a^2\sigma^2}{2} + \frac{a^4}{4}\Big) \quad (17)$$

$$\gamma_{HS}^{(2)} = \frac{\pi\rho^2\sigma^4}{4\beta}\Big[\int_{-{}^1/_2-\bar{a}}^{-{}^1/_2} dv\ (f^+(v) - f^-(v))(v + \bar{a} - 4(v + \bar{a})^3) + \int_{-{}^1/_2}^{-\bar{a}} dv\ (f^+(v) - f^-(v))(\bar{a} - 12v^2\bar{a} - 12v\bar{a} - 12v\bar{a}^2 - 4\bar{a}^3) + \int_{-\bar{a}}^{-\bar{a}/2} dv\ (f^+(v) - f^-(v))(-2v - \bar{a} + 4v^3 + 4(v + \bar{a})^3) + \int_{-\bar{a}}^{-\bar{a}/2} dv\ f^+(v)(2(v + \bar{a}) - 8(v + \bar{a})^3) + \int_{-\bar{a}/2}^{0} dv\ f^+(v)(-2v + 8v^3)\Big] \quad (18)$$

(64) J. G. Kirkwood in "Phase Transition in Solids", R. Smoluchowski, Ed., Wiley, New York, 1951, p 67.

TABLE II: "Ideal Capacitor" Contribution to Surface Tension for Various Values of d

	$\gamma_{EL}^{(1)}$						
$\bar{a}$	$d/\sigma = 0.50$	0.75	1.00	1.25	1.50	1.75	2.00
0.00	0	0	0	0	0	0	0
0.05	−15.367	−22.803	−30.239	−37.675	−45.111	−52.547	−59.983
0.10	−63.453	−93.196	−122.940	−152.683	−182.426	−212.170	−241.913
charged plane[a]	−59.487	−89.230	−118.974	−148.717	−178.460	−208.204	−237.947

[a] For $q_M = 19268.6$ esu/cm^2.

with $v\sigma = {}^1/_2(z_1 + z_2)$ and $\bar{a} = a/\sigma$. We have assumed $\bar{a} < 1$. These two contributions are given in Table I. It is seen that as $\bar{a}$ moves away from zero, the charge due to $\gamma_{HS}^{(1)}$ is overcompensated by the term in $\gamma_{HS}^{(2)}$. Since this term arises from interactions between particles of the salt, it is the same for $-\bar{a}$ as for $\bar{a}$.

The electrostatic contribution to the surface tension, using our assumptions for the $\rho_{ij}^{(2)}$, is conveniently written

$$\gamma_{EL} = \frac{\pi e^2}{2}\int dz_1 \int dz_2 \int_{|z_{12}|}^{\infty} dr_{12}\left(1 - \frac{3z_{12}^2}{r_{12}^2}\right) \times [\rho_+(z_1)\rho_-(z_2)h_{+-}(z_1z_2r_{12}) + \rho_-\rho_+h_{-+} - \rho_+\rho_+h_{++} - \rho_-\rho_-h_{--} - \rho^e(z_1)\rho^e(z_2)] \quad (19)$$

where $h_{ij} = g_{ij} - 1$. The electric charge density ρ^e is $\rho_+ - \rho_- + \rho_M$ and ρ_M, the charge density of the metal, is $q_M\delta(z - d)$. The term in ρ^e, involving no interparticle correlations, is

$$\gamma_{EL}^{(1)} = -\frac{\pi e^2}{2}\int dz_1 \int dz_2 \int_{|z_{12}|}^{\infty} dr_{12}\left(1 - \frac{3z_{12}^2}{r_{12}^2}\right)\rho^e(z_1)\rho^e(z_2) = -(4\pi)^{-1}\int_{-\infty}^{\infty} dz_2\, E(z_2)^2 = -\pi e^2\rho^2\left(\frac{\bar{a}^3\sigma^3}{3} + \bar{a}^2\sigma^2 d\right) \quad (20)$$

The second expression in (20), obtained by integrations by parts and use of the Poisson equation, $4\pi\rho^e e = dE/dz$, is the classical expression for surface tension in terms of the electrostatic field E. The insertion of the electric field for the present problem immediately yields the last expression of (20), which may be written in terms of q by using the formula (6) for a. The rest of γ_{EL} is rewritten by putting $h_{ij} = g_{ij} - 1$, inserting our assumptions for the g_{ij}, and separating contributions of h^S and g^D. Thus

$$\gamma_{EL} = \gamma_{EL}^{(1)} + \gamma_{EL}^{(2)} + \gamma_{EL}^{(3)} + \gamma_{EL}^{(4)}$$

where

$$\gamma_{EL}^{(2)} = \frac{\pi e^2}{2}\int dz_1 \int dz_2 \int_{|z_{12}|}^{\infty} dr_{12}\left(1 - \frac{3z_{12}^2}{r_{12}^2}\right)h^S(r_{12})[\rho_+(z_1) - \rho_-(z_1)][\rho_-(z_2) - \rho_+(z_2)] = -\frac{\pi e^2\rho^2}{16}\int_0^a dr\, r^2h^S(r)$$

$$\gamma_{EL}^{(3)} + \gamma_{EL}^{(4)} = \frac{\pi e^2}{2}\int dz_1 \int dz_2 \int_{|z_{12}|}^{\infty} dz_{12}\left(1 - \frac{3z_{12}^2}{r_{12}^2}\right)g^D(r_{12})\left[\rho_+(z_1)f_+\left(\frac{z_1 + z_2}{2}\right) + \rho_-(z_1)f_-\left(\frac{z_1 + z_2}{2}\right)\right][\rho_+(z_2) + \rho_-(z_2)] \quad (21)$$

TABLE III: Other Electrostatic Contributions to Surface Tension (dyn/cm)

$\bar{a}$	$\gamma_{EL}^{(2)}$	$\gamma_{EL}^{(3)}$	$\gamma_{EL}^{(4)}$
0.00	0	226.83	176.83
±0.05	0.031	225.82	178.14
±0.10	0.248	222.80	171.25

The division into two parts is made to isolate the electroneutrality correction, by writing $f_\pm = 1 + f_\pm - 1$, so that

$$\gamma_{EL}^{(3)} = \frac{\pi e^2}{2}\int dz_1 \int dz_2 \int_{|z_{12}|}^{\infty} dr_{12}\left(1 - \frac{3z_{12}^2}{r_{12}^2}\right)g^D(r_{12}) \times [\rho_+(z_1) + \rho_-(z_1)][\rho_+(z_2) + \rho_-(z_2)] = \frac{\pi e^2\rho^2}{16}\left[\int_0^{\infty} dr\, g^D(r)r^2 + \int_a^{\infty} dr\, g^D(r - a^2/r)^2\right] \quad (22)$$

Finally, $\gamma_{EL}^{(4)}$, which must be evaluated by numerical quadratures, has the expression

$$\gamma_{EL}^{(4)} = \frac{\pi e^2}{2}\int dz_1 \int dz_2 \left\{\rho_+(z_1) \times \left[f_+\left(\frac{z_1 + z_2}{2}\right) - 1\right] + \rho_-(z_1)\left[f_-\left(\frac{z_1 + z_2}{2}\right) - 1\right]\right\}[\rho_+(z_2) + \rho_-(z_2)][G_D^{(0)}(|z_{12}|) - 3z_{12}^2G_D^{(-2)}(|z_{12}|)] \quad (23)$$

where we abbreviate moments of g^D by

$$G_D^{(j)}(x) = \int_x^{\infty} dr\, r^jg^D(r) \quad (24)$$

Expression 20 for $\gamma_{EL}^{(1)}$ corresponds to an idealized capacitor in that interparticle correlations are not present. It is the only term which depends on d, the distance of the charged plane from the density profiles of the ions of the salt. We calculate it for several values of d between ${}^1/_2\sigma$ and 2σ, giving the results of Table II. For this term we use $\bar{a} > 0$ for both positive and negative surface charge, thus keeping constant the distance of closest approach between the metal and an ion of the salt. The contribution of $\bar{a}^3$ is of only minor importance. Without it

$$\gamma_{EL}^{(1)} = -\pi d(2q_M)^2$$

corresponding to the energy of a plane capacitor. Using this with $a = 0.10$, we calculate the last line of Table II. The term in h^S, $\gamma_{EL}^{(2)}$, is easily calculated for $|a| < \sigma$, since $h^s(r)$ is -1 for $r < \sigma$. We have

$$\gamma_{EL}^{(2)} = \frac{\pi e^2\rho^2}{16}\frac{a^3}{3}$$

giving the small contributions tabulated in Table III. The term $\gamma_{EL}^{(3)}$ is, since $g^D(r)$ vanishes for $r < \sigma$

$$\frac{\pi e^2\rho^2}{16}\left[2\int_0^{\infty} dr\, g^D(r) + \int_0^{\infty} dr\, g^D(r)(-2a^2 + a^4r^2)\right]$$

The second moment of $g^D(r)$ is $1/(4\pi\rho)$ and the zeroth and

TABLE IV: Calculated Surface Tensions (dyn/cm)

		$\gamma_{HS} + \gamma_{EL}^{(1)} + \gamma_{EL}^{(2)} + \gamma_{EL}^{(3)}$			$\gamma_{HS} + \gamma_{EL}$		
$\bar{a}$	$d/\sigma =$	0.5	1.0	2.0	0.5	1.0	2.0
0.05		−94.06	−108.93	−138.67	84.08	69.21	39.47
0.10		−139.04	−198.53	−317.50	32.21	−27.28	−146.25

TABLE V: Calculated Surface Tensions and Potential Drops

	charge density,		potential drop, statvolt			surface tension, dyn/cm		
$\bar{a}$	esu/cm²	$d/\sigma =$	0.5	1.0	2.0	0.5	1.0	2.0
0	0.0		0.0	0.0	0.0	97.23	97.23	97.23
±0.05	±9634.3		$\pm 1.62080 \times 10^{-3}$	$\pm 3.1644 \times 10^{-3}$	$\pm 6.2517 \times 10^{-3}$	84.08	69.21	39.47
±0.10	±19268.6		$\pm 3.39567 \times 10^{-3}$	$\pm 6.4832 \times 10^{-3}$	$\pm 12.6577 \times 10^{-3}$	32.21	−27.28	−146.25

minus second moments were evaluated by Pastor[31,65] giving $\gamma_{EL}^{(3)}$ as tabulated in Table III, which represents close to quadratic dependence on $\bar{a}$. The term $\gamma_{EL}^{(4)}$ is also given.

The last term vanishes without the electroneutrality correction, i.e., when $f_+ = f_- = 1$. Thus it is of interest to calculate surface tensions in the absence of $\gamma_{EL}^{(4)}$, as shown in Table IV. The unreasonable negative surface tensions have been discussed previously.[31,32] The electroneutrality correction $\gamma_{EL}^{(4)}$ makes the surface tension positive at the pzc. For large electrode charge one still gets negative values, but one must remember that the actual surface tension of the interface is that of the salt plus that of the metal. The latter can be several hundred dynes/centimeter at the pzc, and, as the interface is charged, additional contributions from the metal may arise. Our results for surface tensions and potential drops are given in Table V.

V. Surface Tensions and Lippmann Equation

The surface tension at the point of zero charge is what we calculate for the free surface, 97.23 dyn/cm. In comparing it to experimental values for the free surface of alkali halides, one should recall that we are assuming there is no double layer for the electroneutral surface, which would hold for equal anion and cation core sizes, whereas the actual cation–anion radius ratio for NaCl is far from 1. The ratios for NaCl, KCl, and RbCl are 0.52, 0.73, and 0.82; surface tensions at 1128 K are 111.3, 92.8 and 86.2 dyn/cm, respectively.[66] The effect of the size asymmetry on surface tension is a matter for subsequent investigation. It may be noted that, if it is important in determining surface structure, it should produce oppositely directed double layers for the free surface (larger ions to the outside of the salt) and for the surface of the salt in the interface (larger ions away from the metal, i.e., toward bulk salt). However, surface energies and surface entropies may well be independent of the *sign* of the surface double layer. Smirnov, Stepanov, and Sharov[67,68] have argued that the metal at the pzc does not alter the surface structure of the salt from that of the free surface, since γ_{free} and $\gamma_{metal-salt}$ change in a parallel way as one goes from one alkali chloride to another. Defining the work of adhesion W^a as the surface tension of the metal alone plus the surface tension of the salt alone minus the interfacial tension of the metal–molten salt interface at the pzc, they find[68] values for W^a of 139 dyn/cm² for Pb in alkali chlorides, 134 dyn/cm² for In, and 105 dyn/cm² for Bi (although experimental errors in the Bi surface tension are large). W^a is quite independent of the alkali cation, and only slightly dependent on the anion.[67] On the other hand, Ukshe et al.[69] have interpreted their electrocapillary measurements in terms of a significant influence of the metal on the top layer of the salt structure. They conclude that each salt has a different structure in the double layer, according to the cation–cation radius ratio.

TABLE VI: Properties of Electrocapillary Curves

$\bar{a}$	d/σ	γ, dyn/cm	q, esu/cm²	V, statvolt
0		97.23		0
0.05	0.5	84.08	9634	0.001 620 8
0.05	1.0	69.21	9634	0.003 164 4
0.05	2.0	39.47	9634	0.006 251 7
0.10	0.5	32.21	19269	0.003 396 0
0.10	1.0	−27.28	19269	0.006 483
0.10	2.0	−146.25	19269	0.126 577

The differential capacitance of the interface[11] is given by $(\partial q/\partial V)_{p,T,\mu}$, where μ represents the bulk chemical potentials of the species, i.e., bulk compositions is to be held constant.[70,71] With stepfunctions for anion and cation densities, the electric field is $2\pi e\rho(z + \bar{a}\sigma)$ for z between $-\bar{a}\sigma$ and 0, $2\pi e\rho\bar{a}\sigma$ for z between 0 and d, and zero elsewhere. Thus

$$V = 2\pi e\rho\bar{a}\sigma(d + \tfrac{1}{2}\bar{a}\sigma) \qquad (25)$$

where $\bar{a}$ is taken positive. These potentials are given in Table VI. With $q = a\rho e/2$ (the convention here is that q is the charge per unit area on the salt and V the electrical potential in bulk salt minus the electrical potential in bulk metal), we get

$$\frac{dq}{dV} = \frac{dq/da}{dV/da} = \frac{\frac{1}{2}\rho e}{2\pi e\rho(d + \frac{1}{2}|a|) + \pi e\rho|a|}$$

Thus the capacitance at the point of zero charge or electrocapillary maximum ($a = 0$) is simply $(4\pi d)^{-1}$, which is the value for an ideal capacitor. Capacitances for $a \neq 0$ are less than ideal value by a factor of $d/(d + |a|)$.

The capacitance $(4\pi d)^{-1}$, equal to 6.935, 3.467, and 1.7337 μF/cm² for $d = 0.5\sigma$, σ, and 2σ, respectively, is much smaller than any of the values measured by Ukshe et al.[69] for Pb–molten salt interfaces. For Pb–NaCl, at 1093 K, a value of 45 μF/cm² is reported, which seems typical of values for molten salts, although there is some question of the importance of Faradaic contributions to the capacity,[72] and of the contribution of the metal as well as of

(65) R. W. Pastor, Thesis, Syracuse University, 1977.
(66) G. Janz, "Molten Salts Handbook", Academic Press, New York, 1967.
(67) V. P. Stepanov and M. V. Smirnov, *Dokl. Phys. Chem.*, **227**, 266 (1976) [translation of *Dokl. Akad. Nauk SSSR*, **227**, 403 (1976)].
(68) M. V. Smirnov, V. P. Stepanov, A. F. Sharov, and V. I. Minchoenko, *Sov. Electrochem.*, 8, 961 (1972) [translation of *Electrokhimiya*, 8, 994 (1972)].
(69) E. A. Ukshe, N. G. Bukun, D. J. Leikis, and A. N. Frumkin, *Electrochim. Acta*, **9**, 437 (1964).
(70) A. Sanfeld, "Introduction to the Thermodynamics of Charged and Polarized Layers", Wiley-Interscience, London, 1968.
(71) J. P. Badiali and J. Goodisman, *J. Phys. Chem.*, **79**, 223 (1975).

the salt. To obtain 45 $\mu F/cm^2$ from our model, we would need $d = 0.077\sigma$. It appears that the above calculation is not capable of accounting for the measured values. However, this calculation obtained q and V by assuming stepfunction densities for the ions; as discussed below, these are not the only one-particle densities one could use.

According to the Lippmann equation[11,70,71,73] the surface charge density can be obtained from the electrocapillary curve:

$$q = -(\partial\gamma/\partial V)_{p,T,\mu} \tag{26}$$

Thus, we use the data of Table VI for $\bar{a} = 0$ and ± 0.05 to write

$$\gamma = \gamma_{pzc} - bV^2 \tag{27}$$

For the three values of d, we find $b = 5.0057 \times 10^6$, 2.7982×10^6, and 1.47785×10^6 cm^{-1}, respectively. The resulting capacitances at the point of zero charge are given by

$$C = -\partial^2\gamma/\partial V^2 = 2b$$

In mks units, the three values of b give capacitances of 11.124, 6.218, and 3.2844 $\mu F/cm^2$, about twice the ideal values of $^1/_4\pi d$, and closer to measured values. Note that the electroneutrality correction $\gamma_{EL}^{(4)}$, extremely important in getting a reasonable result for surface tension, is much less important for the electrical capacitance, given by the second derivative of the surface tension with potential. Apparently, the electroneutrality correction is relatively constant with electrode charge. If, using the data for $\bar{a} = 0$ and ± 0.05, we write γ as a parabolic function of a, the second derivative, for $d/\sigma = 1$, is 23 464 dyn/cm without $\gamma_{EL}^{(4)}$ and 22 416 dyn/cm with this correction.

The Lippmann equation is not satisfied by our model: the charge densities according to (26) and (27) approach twice the value obtained from the stepfunction charge densities. The reason for the discrepancy is found on examination of $\gamma_{EL}^{(1)}$, which is the largest term in γ which varies with charge. For d much larger than $|a|$, it becomes

$$\gamma_{EL}^{(0)} = -\pi e^2\rho^2 a^2 d = -4\pi q^2 d = -V^2/4\pi d \tag{28}$$

Note that the field energy of an ideal capacitor is[74]

$$E_c = \frac{1}{8\pi}\int_0^d E^2\, dz = 2\pi q^2 d = V^2/8\pi d$$

with E the electric field, which differs from $\gamma_{EL}^{(0)}$ in that the latter is a free energy, involving the work necessary to separate charges in forming the double layer, as discussed in Chapter 17 of ref 70 and elsewhere.[75] Differeniation of (28) gives

$$\frac{d\gamma_{EL}^{(1)}}{dV} = \frac{-V}{2\pi d} = -2q$$

The violation of the Lippmann equation is related to the lack of mechanical equilibrium.[71,73,75] The Born–Green–Yvon equation, or mechanical equilibrium condition, is

$$\frac{d\rho_i^{(1)}(z)}{dz} = -\frac{1}{kT}\sum_j \int \frac{du_{ij}(|\vec{r} - \vec{r}'|)}{dz}\rho_{ij}^{(2)}(\vec{r}, \vec{r}')\, d\vec{r}' \tag{29}$$

for a system in which all forces are central. It relates the one- and two-particle distributions and, by relating the corresponding contributions to the pressure, guarantees the constancy of the normal component of the pressure through the interface. When this constancy is used in conjunction with the formula (14) for the surface tension, which involves[70,76] the difference between tangential (x component) and normal (z component) pressure, a new formula is obtained. With p_h representing the (isotropic) pressure of the homogeneous phase, we have

$$\gamma = -\int dz_1\, (p^T(z_1) - p^N(z_1)) = \int dz_1\, (p_h - p^T(z_1)) =$$
$$\int_{-\infty}^{0} dz_1 \left[kT\rho - \tfrac{1}{2}\sum_{ij}\int d\vec{r}_{12}\, (\tfrac{1}{2}\rho)^2 g_{ij}^b(r_{12}) u'_{ij}(r_{12}) x_{12}^2/r_{12}\right]$$
$$- \int dz_1 \left[kT\sum_i \rho_i^{(1)}(z_1) - \tfrac{1}{2}\sum_{ij}\int d\vec{r}_{12}\, \rho_{ij}^{(2)} u'_{ij}(r_{12}) x_{12}^2/r_{12}\right] \tag{30}$$

where g_{ij}^b is the bulk correlation function, depending only on r_{12}. This gives γ in terms of "surface excess" densities and two-particle distributions, i.e.

$$\gamma = kT\left(\frac{\rho}{2}\right)a - \gamma'_{EL} - \gamma'_{HS}$$

The contribution of the electrostatic forces may be calculated as in eq 19–24. The term corresponding to $\gamma_{EL}^{(4)}$ is not expected to contribute much. In the remaining electrostatic terms

$$\gamma'_{EL} = \frac{-\pi e^2\rho^2}{2}\left(\frac{a^3}{3} + a^2 d\right) +$$
$$\frac{\pi e^2\rho^2}{8}\left[\frac{a^4}{6\sigma} + a^2\sigma - \frac{2a^3}{3} + \int_a^\infty dr\, h^s(r)\left(\frac{a^4}{6r^2} - a^2\right)\right] -$$
$$\frac{\pi e^2\rho^2}{2}\left[\frac{a^2}{4}G_D^{(0)}(0) + \frac{2a}{3}G_D^{(1)}(0) + \frac{13a^4}{48}G_D^{(2)}(0)\right]$$

the first term, which is the largest, is just half of $\gamma_{EL}^{(1)}$, so differentiation with respect to V will give the correct q. Unfortunately, consideration of the contribution of the hard-sphere potential to surface tension shows that (30) would give totally unreasonable surface tensions.

Mechanical equilibrium and consistency among these surface tension expressions may be restored to our model by using, when surface charges and potentials are discussed, one-particle distributions $\rho_i^{(1)}$ generated from the two-particle distributions $\rho_{ij}^{(2)}$ of our model by eq 29. These $\rho_i^{(1)}$ are consistent with the $\rho_{ij}^{(2)}$ in the sense that (30) will lead to the same surface tension as (14), and the pressure normal to the interface will be independent of z. Since we have calculated γ using (14), which requires only the $\rho_{ij}^{(2)}$, the surface tensions will not be changed; if we use (30) to calculate the surface tension, we insert $\rho_i^{(1)}$ calculated from (29) and $\rho_{ij}^{(2)}$ as before. There is still an inconsistency in that the two-particle ion–metal distributions, for which there is no correlation, are constructed with stepfunctions rather than the true one-particle distributions.

In order that the integration of (29) to give one-particle densities make sense, $d\rho_i^{(1)}/dz$ must vanish for $z \to -\infty$. This can be shown by invoking the short range of u_{HS}, $g^S - 1$, and g^D. The charge density for calculation of electrical properties is now given by

$$\rho(z) = \sum_i e_i\rho_i(z) = \rho(-\infty) + \sum_i e_i \int_{-\infty}^{z} dz' \frac{d\rho_i^{(1)}(z')}{dz'} \tag{31}$$

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where $d\rho_i^{(1)}/dz$ is given by (29); $\rho(-\infty)$ of course vanishes. The charge density at $z = 0$ is 6.65170 esu/cm^2. The calculated value of q (charge on the salt) depends on x, the value of z at which we cut off the $\rho_i^{(1)}$:

$$q = \int_{-\infty}^{x} dz\ \rho(z) = -\sum_i e_i \int_{-\infty}^{x} dz\ (z - x)(d\rho_i^{(1)}/dz) \qquad (32)$$

We may choose the value of x to make q equal to the value implicit in our $\rho_{ij}^{(2)}$, i.e.

$$\frac{a\rho}{2} = -2\pi\sum_i e_i \int_{-\infty}^{x} dz\ (z - x)(-kT)^{-1} \sum_j \int_{-\infty}^{\infty} dz'\,(z - z') \times \int_{|z-z'|}^{\infty} dr\ u'_{ij}(r)\rho_{ij}^{(2)}(zz'r) = (2\pi e/dT) \times \int_{-\infty}^{x} dz\ (z - x) \int_{-\infty}^{\infty} dz'\,(z - z') \times \int_{|z-z'|}^{\infty} dr\ [u'_{HS}g^S(\bar{\rho}_+ - \bar{\rho}_-)(\bar{\rho}_+ + \bar{\rho}_-) - u'_{HS}g^D(\bar{\rho}_+ + \bar{\rho}_-) \times (\bar{\rho}_+ - \bar{\rho}_-) - (e^2/r^2)g^S(\bar{\rho}_+ + \bar{\rho}_-)(\bar{\rho}_+ - \bar{\rho}_-) + (e^2/r^2)g^D(\bar{\rho}_+ + \bar{\rho}_-) + (e^2/r^2)(\bar{\rho}_+ + \bar{\rho}_-)(z' - d)] \qquad (33)$$

Here, we have put $f_\pm = 1$ since the electroneutrality factors make only a small contribution to the change of surface tension with potential. The notation $\bar{\rho}_+$ and $\bar{\rho}_-$ is now used to distinguish the stepfunctions appearing in $\rho_{ij}^{(2)}$ from the one-electron densities now being generated and used in q and V. In a product of two $\bar{\rho}_i$ (i = + or −) the first factor is a function of z and the second of z'. The right side of (33) may be reduced, after considerable algebra, to an expression involving the moments and contact values of g^S and g^D. Then the solution of (33) leads to $x = -0.39497\sigma$.

The potential drop across the entire interface, with contributions from the charge density of the metal as well as from the ions of the salt, may be written

$$V(\infty) - V(-\infty) = -4\pi \int_{-\infty}^{\infty} dz \int_{-\infty}^{z} dz'\,\rho(z') = -4\pi\left[qd + \int_{-\infty}^{x} dz \left(\frac{z^2}{2} - \frac{x^2}{2}\right)\sum_i e_i \frac{d\rho_i^{(1)}}{dz} \right]$$

The value of the integral after insertion of (29) is 1.20318×10^{-4} esu/cm. Therefore, for $d = 0.5\sigma$, σ, and 2σ, we have potential drops of 3.0556×10^{-3}, 4.5992×10^{-3}, and 7.6864×10^{-3} statvolts ($a = 0.05\sigma$). Then the coefficient for the parabola of γ in V^2 (eq 27) becomes, for the three cases, 1.4084×10^6, 1.3247×10^6, and 0.9775×10^6 cm^{-1}. The capacitances become 3.1298, 2.9437, and 2.1725 μF/cm^2, even lower than those previously calculated. The charge densities calculated from the γ–V parabola are 8607, 12 186, and 15 028 esu/cm^2.

The molecular dynamics calculations of Heyes and Clarke,[20] for charged hard spheres near a wall, model molten KCl. Although surface tensions were not reported, a value for capacity was derived from surface charges and potential drops, as computed from the charge densities. The value of 50–70 μF/cm^2 is of the right size, although it was stated that the system is far from the pzc, and that errors in this quantity are large.

We may also compare our results with what one obtains from the Gouy–Chapman model. Apparently, the short-range interionic forces and correlations, which are not considered, lead to corrections which cancel, as seems to occur in the same calculations on the related Debye–Hückel model,[77] leading to satisfaction of the Lippmann equation. In the Gouy–Chapman model, the one-particle densities are assumed to vary according to a Boltzmann distribution in the average electric potential

$$\rho_i^{(1)} = \bar{\rho}_i e^{-e_i\psi/kT} \qquad (34)$$

where $\bar{\rho}_i$ is the value of the density in the bulk ($z \to -\infty$) and e_i the charge of the ith species. Combining (34) with the Poisson equation for the charge density ρ, with dielectric constant unity

$$4\pi\rho = \vec{\nabla}\cdot\vec{E} = -\nabla^2\psi \qquad (35)$$

leads to the Poisson–Boltzmann equation which may be solved for ψ and hence the $\rho_i^{(1)}$. Since short-range forces are ignored in thiis model, the surface tension of eq 15 reduces to γ_{EL}, and, since short-range correlations are also ignored, one can take $h_{ij} = 0$ in eq 19; the result may be written[71]

$$\gamma = -1/(4\pi) \int E^2\, dz \qquad (36)$$

For a 1:1 salt with bulk densith $\rho/2$ for anions and cations and dielectric constant unity, the surface tension of the Gouy–Chapman model may be given explicitly[73,77] as a function of ΔV. Letting $W = e\Delta V/4kT$ and $\kappa^2 = \rho e^2/kT$, we have

$$\gamma = \int_{-\infty}^{0} E^2\, dz = -2\kappa(2kT/e)^2 \sinh^2 W \qquad (37)$$

For our salt, the Debye length $1/\kappa$ is 0.463 193 Å^{-1}. The surface charge on the salt is

$$Q = \int_{-\infty}^{0} \rho\, dz = (4kT\kappa/e) \sinh W \cosh W \qquad (38)$$

To have $Q = 9634.3$ esu/cm^2, we require $W = 0.0343808$, which corresponds to $\Delta V = 4.45903 \times 10^{-5}$ statvolts and $\gamma = -0.2147137$ erg/cm^2. Following our procedure of fitting the results for $Q = 0$ and ± 9634.3 esu/cm^2 to a parabola, we have

$$\gamma = \gamma_0 - 1.079889 \times 10^8 \Delta V^2$$

so $d\gamma/dV = 9630.5$ esu/cm^2 for $\Delta V = 4.45903 \times 10^{-5}$, the deviation from 9634.3 esu/cm^2 being due to the fact that (37) is not precisely a parabola in W. The capacitance is 2.159778×10^8 cm^{-1} or 239.975 μF/cm^2. More precisely, we use (38) to get the capacitance as

$$dQ/d\Delta V = \kappa(\cosh^2 W + \sinh^2 W)$$

which at $W = 0$ is just κ, or 239.881 μF/cm^2. The value is, as previously mentioned, much too high.

VII. Conclusion

The initial purpose of performing these calculations was to ascertain whether one could describe the charged interface of a molten salt (in contact with a charged wall representing the metal) by invoking the same simple assumption for the ion–ion distributions that gave reasonable surface tensions for the neutral surface. Additional assumptions are required for the salt–metal two-particle distribution, and we assumed no correlation. For the charged interface, one is interested in the potential difference between inside and outside the surface, and how it changes as the surface charge changes (electrocapillary curve). The capacities obtained are much too low. However, their calculation requires surface charges and potential drops which, unlike the surface tension as given by the Kirkwood–Buff formula, require the one-particle distributions $\rho_i^{(1)}$. Since the $\rho_i^{(1)}$ assumed were inconsistent with the $\rho_{ij}^{(2)}$, different theoretically equivalent surface tension formulas could give quite different results. A further inconsistency exists between the surface charges

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derived from the Lippmann equation and those calculated from the $\rho_i^{(1)}$.

The first kind of inconsistency is removed by maintaining the $\rho_{ij}^{(2)}$ and using the equation of mechanical equilibrium to derive $\rho_i^{(1)}$ from the $\rho_{ij}^{(2)}$. Different surface tension formulas then give the same results, and mechanical equilibrium is assured in the region where $\rho_i^{(1)}$ and $\rho_{ij}^{(2)}$ are nonzero. Since $\rho_i^{(1)}$ must be truncated to assure the correct surface charge, a new inconsistency appears, as no repulsive interaction between metal and salt particles (which would make $\rho_i^{(1)}$ go to zero) is introduced into the calculations. Furthermore, if one wants to assume no correlation between particles of the metal m and ions of the salt i, the two-particle distribution $\rho_{im}^{(2)}$ should be $\rho_i^{(1)} \times \rho_m^{(1)}$, with $\rho_i^{(1)}$ the same one-particle densities used for calculation of electrical properties. Inserting this into the mechanical equilibrium condition yields a more complicated integral equation for the $\rho_i^{(1)}$, solution of which has not been attempted here.

The capacities calculated with $\rho_i^{(1)}$ derived from mechanical equilibrium are still quite small compared with those reported experimentally for the molten salt–metal surface. The Lippmann equation can be satisfied only for one choice of the distance of closest approach of salt ions to the metal. To help understand the origin of the problem, we considered the Gouy–Chapman model, which, ignoring nonelectrostatic interactions and interparticle correlations, satisfies the mechanical equilibrium condition as well as the Lippmann equation. For a molten salt in contact with a charged wall, this model gives capacities which are much too high. When a region free of ions (Stern layer) is introduced between the region of the salt ions and the charged surface (metal), the potential drop across the interface is increased with no change in the surface charge, thus reducing the capacity. However, the Lippmann equation is no longer satisfied. As in our model, we now have an ionic distribution which drops to zero within the region of the interface, implying a repulsive force, without inclusion of such a force in the surface tension calculation. Again we conclude that a consistent treatment of such forces is required in order for a model to satisfy the Lippmann equation.

Since this equation is easily demonstrated thermodynamically, a few words are appropriate about why we are interested in finding it in our model. The equation as generally stated involves the total surface charge density of the interface and the potential difference between homogeneous regions on either side of the interfacial region. A model gives these quantities specific meaning by supplying information about the charge distributions, from which total density and potential drop are calculable. The charge distribution is also related through the mechanical equilibrium condition to the two-particle distribution, which may be used to calculate the surface tension. From this point of view, the satisfaction of the Lippmann equation is a necessary condition on the two-particle distributions, which describe the correlation due to the interparticle forces.

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Nucleophilic Aromatic Substitution in Microemulsions

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The rate constants of reaction of 2,4-dinitrofluorobenzene (DNF) with OH^- in microemulsions of *n*-octane, *tert*-amyl alcohol, and cetyltrimethylammonium bromide (CTABr) and in micelles of CTABr and *tert*-amyl alcohol can be treated quantitatively by using a pseudophase ion-exchange model and the second-order rate constants in the microemulsion or micelle droplets are larger than that in water, but much smaller than those in moist tertiary alcohols. Reactions of DNF and 2,4-dinitrochlorobenzene (DNC) in microemulsions or micelles containing primary alcohols (*n*-butyl or benzyl alcohol) give largely ethers as products, and the ethers slowly react giving the 2,4-dinitrophenoxide ion. These reactions of DNF and DNC are faster than reactions with OH^- in water but are much slower than those in the alcohols. Qualitatively, the relative apparent nucleophilicities of hydroxide and alkoxide ion in the micelle or microemulsion droplet are similar to those in the absence of surfactant. Anionic microemulsions of sodium lauryl sulfate (NaLS) inhibit reactions, but to smaller extent than anionic micelles in water.

Microemulsions are transparent dispersions containing water, an oil, a surfactant, and a cosurfactant, which is usually a medium chain length alcohol.[1,2] The formation of microemulsions in the absence of surfactant has been reported[3] (cf. ref 2). Reactions can be carried out in these media, and they probably take place in the microemulsion droplets;[3,4] and in some systems the cosurfactant may be the active reagent.[4-6] This behavior has been observed in dephosphorylation at high pH, where the nucleophile is alkoxide ion from the alcohol or an ethylene oxide derived surfactant.[4,6]

The reaction of 2,4-dinitrochlorobenzene (DNC) with *n*-hexylamine occurs readily in microemulsions with an

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