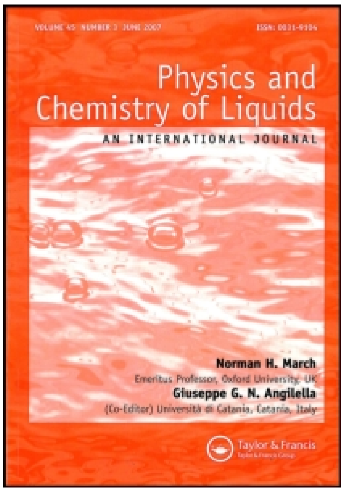

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# Dependence of Capacitance of Metal-Molten Salt Interface on Local Density Profiles Near Electrode

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The mean spherical approximation applied to a metal-molten salt interface is generalized to take further account of the local density profiles near the electrode. The temperature dependence of the differential capacitance is shown to arise, in large measure from such local structure. However, the hard wall assumption for the electrode is retained and this must be kept in mind in comparing our model results with experiment.

## 1 INTRODUCTION

In a previous paper,[1] we applied the mean spherical approximation to calculate the differential capacitance, and its temperature dependence, of the metal-electrolyte interface. This calculation was based on an admittedly simple model in which the metal electrode was replaced by a hard wall without image forces. Less drastically, the molten salt was treated as a statistical mechanical assembly of charged hard spheres with suitably chosen radii in a dielectric continuum.

The main conclusions were:

a) The magnitude of the capacitance at the point of zero charge was in approximate quantitative agreement with available measurements.[2]

b) The temperature dependence was found to be weak, whereas experiment showed that, for the metal-molten salt interface, and in contrast with the metal-aqueous electrolyte interface, the capacitance increased with increasing temperature.

As to point (b) above, a phenomenological correction was proposed to take account of the "softness" of the metal electrode. While this was shown to lead to the possibility of correct temperature dependence of the capacitance, interest nevertheless remains as to whether the mean spherical approximation is correctly describing the temperature dependence of the hard wall model described above. Therefore, in this paper, we have investigated alternative, though related, approaches to the capacitance of the hard wall model.

## 2 DEPENDENCE OF CAPACITANCE ON THE LOCAL IONIC DENSITY PROFILES

In the previous work, we wrote the capacitance at the point of zero charge, $C_0$, in the mean spherical approximation, as

$$C_{0(\mathrm{MSA})}^{-1} = -\frac{4\pi e n}{\varepsilon}\int_0^\infty \mathrm{d}z\, z[\Delta g_{01}(z) - \Delta g_{02}(z)], \tag{2.1}$$

where $n$ is the ionic density, $\varepsilon$ the dielectric constant accounting for electronic polarization of the ions and $\Delta g_{0i}(z)$ are the changes in the wall-ion pair correlation functions induced by placing unit positive charge per unit area on the wall. Equation (2.1) is already written in a form appropriate to a $1-1$ electrolyte. A derivation of the final MSA formula is given in the Appendix.

Though the deviations of the pair functions $\Delta g_{0i}$ from the values $g_{0i}^0(z)$ appropriate to the uncharged wall evidently reflect this local structure, nevertheless the formula (2.1), depending, of course, on the assumptions of the mean spherical approximation, contains the temperature mainly through:

i) The local behaviour of $\Delta g_{0i}(z)$, near the electrode;

ii) Long-range oscillatory effects reflecting charge ordering in the molten salt.

These two effects lead to opposed temperature dependences, which together yield a weak dependence of $C_0$ on $T$. This dependence is a slow decrease of $C_0$ with increasing $T$, in qualitative disagreement with the data[2] on metal-molten salt interfaces.

We have therefore considered further the possibility that the local structure $g_{0i}^0(z)$ in the absence of charging should appear in any final formula for the capacitance $C_0$ of the hard wall model.

### 2.1 Exponential approximation

A way to approach this problem is to make use of a variant of the mean spherical approximation which has been proposed by Blum,[3] and by Henderson and Blum.[4] This treatment writes the pair functions $g_{0i}(z)$ in the presence of surface charge density $q$ on the wall as

$$g_{0i}(z) = g_{0i}^0(z) \exp[q\Delta g_{0i}(z)], \tag{2.2}$$

to be compared with the mean spherical approximation which yields

$$g_{0i}(z) = g_{0i}^0(z) + q\Delta g_{0i}(z). \tag{2.3}$$

We stress that, in the ansatz (2.2), $g_i^0(z)$ and $\Delta g_{0i}(z)$ are still the mean spherical approximation findings.

Eq. (2.1) is then obviously modified to read

$$C_{0(\exp)}^{-1} = -\frac{4\pi en}{\varepsilon}\int_0^\infty \mathrm{d}z\, z[g_{01}^0(z)\Delta g_{01}(z) - g_{02}^0(z)\Delta g_{02}(z)]. \tag{2.4}$$

This formula evidently introduces the local structure of the uncharged problem directly into the formula for the capacitance of the interface.

The disadvantage of the above exponential ansatz, already known in Refs. 3 and 4, is the difficulty with charge neutrality. By this is meant that the charge induced in the molten salt does not exactly compensate the charge on the wall. Bearing in mind this limitation, it is nevertheless clear that formula (2.4) has some merits over the mean spherical approximation to $C_0^{-1}$ in Eq. (2.1) when one comes to study the temperature dependence, and this is the main point we want to stress in the present paper.

### 2.2 Proposed interpolation between formulae (2.1) and (2.4)

As will become apparent from the calculations reported in Section 3 below, the local way in which $g_{0i}^0(z)$ has been introduced into the formula for $C_0^{-1}$ is too drastic. A possible procedure is to introduce non-local effects into the formula for $C_0^{-1}$ by writing

$$\overline{g_{0i}^0}(z) = 1 + \int_0^\infty \mathrm{d}z'\, F(z - z')[g_{0i}^0(z') - 1]. \tag{2.5}$$

Our proposal is then to replace $g_{0i}^0(z)$ in Eq. (2.4) by $\overline{g_{0i}^0}(z)$. Evidently the precise formula (2.4) corresponds to choosing $F(z - z') = \delta(z - z')$, whereas (2.1) corresponds to choosing $F(z - z')$ as zero.

A possible interpolation formula might be

$$F(z - z') = \frac{1}{\sqrt{2\pi}\, l} \exp\left[ - \frac{(z - z')^2}{2l^2} \right]. \tag{2.6}$$

Evidently $l \to 0$ reproduces the $\delta$ function limit, while $l$ tending to the size of the system reproduces the mean spherical approximation (2.1).

Obviously, choosing $l$ of the order of an Å, one gets results somewhat between the predictions of formulae (2.1) and (2.4). The length $l$ will depend on temperature and can be chosen to take care of charge neutrality in $\overline{g_{0i}^0}(z)$. It turns out that this condition can be satisfied by a set of values for $l$.

### 2.3 Correction of exponential approximation for charge neutrality

An alternative procedure, leading in the same direction, is to introduce empirical corrections for charge neutrality[4,5] in Eq. (2.2). The spatial distribution of the compensating charge is evidently crucial for calculating induced dipole moments and hence the capacitance. Aiming only at qualitative effects, one can simply replace Eq. (2.2) by

$$\left.\begin{aligned} g_{0+}(z) &= (1 - \lambda) g_{0+}^0(z) \exp[q \Delta g_{0+}(z)] + \lambda \\ g_{0-}(z) &= (1 + \lambda) g_{0-}^0(z) \exp[q \Delta g_{0-}(z)] - \lambda \end{aligned}\right\} \tag{2.7}$$

where $\lambda$ is a parameter which is fixed by imposing charge neutrality. This yields a dependence of $\lambda$ on the surface charge $q$, and although $\lambda$ vanishes for $q = 0$, its derivative $\mathrm{d}\lambda/\mathrm{d}q$ enters in determining $C_0$.

## 3 NUMERICAL RESULTS AT THE POINT OF ZERO CHARGE

From formula (2.4), we have calculated $C_0^{-1}$ vs $T/T_m$, where $T_m$ is the melting temperature, for molten chlorides and salts of potassium. The capacitance is now found to increase substantially with increasing temperature, as seen from Figure 1. However, $C_0$ is much smaller than the observed values, by a factor which can be as large as an order of magnitude.

Common ground with the mean spherical approximation is found in the strong dependence of $C_0$ on the size of the cation and in the insensitivity to the radius of the anion, these latter features being in accord with experiment.

A comparative illustration of the various procedures presented in Section 2 for $C_0$ and $d \ln C_0/\mathrm{d}T$ is given in Table I for the case of potassium iodide.

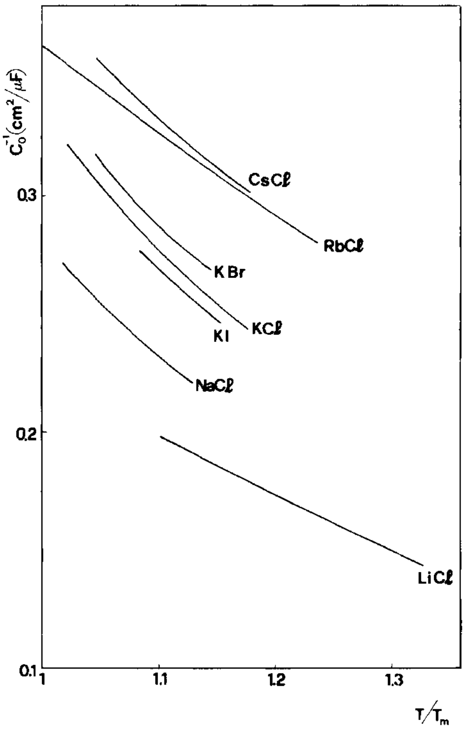

FIGURE 1 Inverse capacitance at the point of zero charge versus temperature (in units of the melting temperature $T_m$) for the hard wall-molten salt interface in the exponential approximation, Eq. (2.4).

TABLE I

Capacitance of metal-molten salt interface at various temperatures†

| $T(K)$ | 1012 | | 1053 | | 1101 | |
|---|---|---|---|---|---|---|
| | $C_0$ | $10^3 \frac{d \ln C_0}{dT}$ | $C_0$ | $10^3 \frac{d \ln C_0}{dT}$ | $C_0$ | $10^3 \frac{d \ln C_0}{dT}$ |
| MSA, Eq. (2.1) | 25.7 | −0.44 | 25.2 | −0.48 | 24.6 | −0.53 |
| EXP, Eq. (2.4) | 3.5 | 1.4 | 3.7 | 1.6 | 4.1 | 1.8 |
| Eq. (2.5), $l \simeq 0.80$ Å | 7.7 | 1.4 | 8.1 | 1.4 | 8.7 | 1.5 |
| Eq. (2.5), $l \simeq 1.15$ Å | 10.6 | 0.45 | 10.8 | 0.42 | 11.0 | 0.39 |
| Eq. (2.7) | 12.6 | 1.2 | 13.3 | 1.4 | 14.3 | 1.6 |
| Expt. | 30.5 | 0.94 | 31.7 | 1.04 | 33.4 | 1.15 |

† $C_0$ is in $\mu F/cm^2$. The experimental values refer to the liquid lead-potassium iodide interface and are taken from Graves.[2] The other values are calculated for the hard wall-charged hard spheres interface, the parameters of the charged hard spheres liquid being chosen to simulate potassium iodide.

Evidently, in all these schemes the calculated capacitance is small compared with the result of the mean spherical approximation and with the observed value. On the other hand, the sign of $d \ln C_0/\mathrm{d}T$ is now consistently positive.

## 4 VARIATION OF DIFFERENTIAL CAPACITANCE WITH SURFACE CHARGE DENSITY

The simple scheme described in Section 2.3 above can also be applied to calculate the differential capacitance away from the point of zero charge. The results for a model hard wall-sodium chloride interface are reported in Figure 2 at two temperatures, the range of surface charge densities representing a variation of interfacial potential by several tenths of a Volt.

The rather strong asymmetry in the ionic sizes for this system (with a radius ratio $r_+/r_- \simeq 0.7$) reflects itself in a rather minor shift of the minimum of the differential capacitance away from the point of zero charge. The symmetric increase of the capacitance away from its minimum is in qualitative agreement with experimental data[2] for the interface between liquid lead and LiCl–KCl mixtures. The calculated curves at the two temperatures are seen to be essentially similar except for a shift in the position of the minimum. However, when the capacitance is plotted as a function of potential rather than of surface charge density, the upper curve clearly becomes steeper, this being again in qualitative accord with experiment.

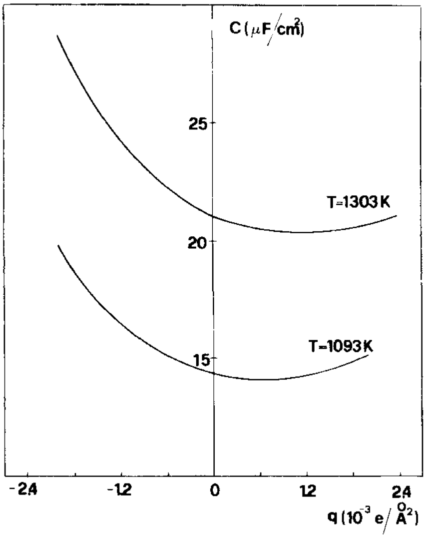

FIGURE 2 Differential capacitance versus surface charge density for the hard wall-molten NaCl interface in the exponential approximation corrected for charge neutrality, Eq. (2.7).

## 5 SUMMARY AND CONCLUSION

The thrust of the present paper has been to modify the approximate statistical mechanics of the hard wall-molten salt problem. We have sought a formula for the capacitance at the point of zero charge which transcends the mean spherical approximation (2.1). One modification, proposed in Refs. 3 and 4, yields Eq. (2.4), but present evidence strongly suggests, in contrast to (2.1), that (2.4) is overemphasizing the role of the local structure of the uncharged interface near the wall on both $C_0^{-1}$ and its temperature dependence.

Of course, presently we have no means of deciding exactly how good the hard wall model itself is, in relation to experiment. However, pressing the phenomenological discussion of Ref. 1 on the "softness" of the electrode, it seems clear to us that this should result in a contribution to $C_0$ which increases with increasing temperature. Therefore, we feel for the hard wall model, that the results of the mean spherical approximation are already somewhat more realistic than those of the exponential model.

We have next explored other approximations that are in essence intermediate between the above two extremes. We have seen that some qualitative features of the model are in broad accord with experiment.

Further progress is clearly to be sought from computer simulation of the hard wall model. This direction is currently being explored.

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# Appendix

## CAPACITANCE AT THE POINT OF ZERO CHARGE IN THE MEAN SPHERICAL APPROXIMATION

It was noted in Ref. 1 that Eq. (2.1) for $C_{0(\mathrm{MSA})}^{-1}$ leads, upon numerical evaluation, to the expression

$$C_{0(\mathrm{MSA})} = \frac{\varepsilon}{4\pi}\, 2\Gamma, \tag{A1.1}$$

where the quantity $2\Gamma$ is a generalization of the Debye inverse screening length. We present below an analytic derivation of Eq. (A1.1), extending to arbitrary values of the ionic radius ratio the proof given by Blum[3] for equal ionic radii.

It is convenient to consider for this purpose an ion in the liquid of charged hard spheres as a probe of the electrical potential in a Debye-type charging process. This is formally done by considering the presence of a third ionic species in the 1 − 1 electrolyte. The third species consists of ions with charge $Z_3 e$, diameter $\sigma_3$ and density $n_3$ which will be allowed to vanish in such a way that $n_3\sigma_3^3 \to 0$.

The potential drop between the surface of the probe and infinity is

$$\phi(\tfrac{1}{2}\sigma_3) - \phi(\infty) = \frac{Z_3 e}{\varepsilon}\int_{1/2\sigma_3}^{\infty}\frac{\mathrm{d}r}{r^2} + \frac{4\pi e}{\varepsilon}\sum_i n_i Z_i \int_{1/2\sigma_3}^{\infty}\frac{\mathrm{d}r}{r^2}\int_{1/2\sigma_3}^{\infty}\mathrm{d}r'\, r'^2 h_{3i}(r'), \tag{A1.2}$$

where $h_{3i}(r)$ is the total correlation function between the probe and ions of species $i$. On account of charge neutrality, Eq. (A1.2) can be written

$$\phi(\tfrac{1}{2}\sigma_3) - \phi(\infty) = \frac{2Z_3 e}{\varepsilon\sigma_3} + \frac{2e}{\varepsilon}\sum_i n_i Z_i J_{i3}, \tag{A1.3}$$

where

$$J_{i3} \equiv 2\pi\int_0^{\infty}\mathrm{d}r\, r h_{i3}(r). \tag{A1.4}$$

The MSA yields explicit expressions for the quantities $J_{ik}$, leading to[6]

$$\sum_i n_i Z_i J_{i3} = N_3 - \frac{\pi}{6}\sum_i n_i\sigma_i^3 N_i - \frac{\pi}{4}\sum_i n_i Z_i \sigma_i^2, \tag{A1.5}$$

where

$$N_i = -\left(\Gamma Z_i + \frac{\pi}{2\Delta}\sigma_i P_n\right)\Big/(1 + \Gamma\sigma_i), \tag{A1.6}$$

$\Delta$, $P_n$ and $\Gamma$ being quantities which are known from the MSA solution. Taking now the limit $n_3 \to 0$ with $n_3\sigma_3^3 \to 0$, these quantities take the values appropriate to the pure $1-1$ electrolyte and one easily finds from the above expressions

$$\phi(\tfrac{1}{2}\sigma_3) - \phi(\infty) = \frac{2eZ_3}{\varepsilon\sigma_3(1 + \Gamma\sigma_3)} + (\text{terms independent of } Z_3). \quad \text{(A1.7)}$$

By differentiating this expression with respect to $Z_3 e$ we find the capacitance of the probe as

$$C = \tfrac{1}{2}\varepsilon\sigma_3(1 + \Gamma\sigma_3). \quad \text{(A1.8)}$$

The case of a hard wall is recovered by taking the capacitance of the probe per unit area and letting $\sigma_3 \to \infty$, which yields Eq. (A1.1).