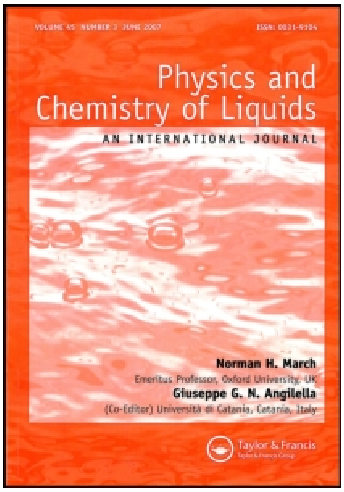

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Effect of Microscopic Structure of Metal Electrode on Capacitance of Metal-Molten Salt Interface

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Effect of Microscopic Structure of Metal Electrode on Capacitance of Metal-Molten Salt Interface

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A brief discussion of both ionic structure and electron spill-out from the metal electrode is given, in relation to the capacitance of the metal-molten salt interface. A microscopic basis can thereby be given to the earlier phenomenological treatment of the capacitance of this interface.

1 INTRODUCTION

In previous work,[1] we have proposed that the capacitance C_0, at the point of zero charge, of the metal-molten salt interface, can be usefully related to a statistical mechanical model in which the molten salt is in contact with a charged hard wall. The capacitance of this model system, again at the point of zero charge, is

$$C_0^m = \frac{\varepsilon}{4\pi} l_s^{-1} \tag{1.1}$$

where ε is the electronic dielectric constant of the molten salt, while l_s is the ionic screening length.

Then C_0 was constructed from a phenomenological modification, via a length $\Delta\sigma$ representing the penetration of molten alkali halide ions into the metal surface, as

$$C_0 = \frac{\varepsilon}{4\pi} l_s^{-1}/(1 - \Delta\sigma/l_s) \tag{1.2}$$

Estimates of $\Delta\sigma$ from experiment clearly involve knowledge of the screening length l_s, associated with the model hard wall system. For example, calculations using the mean spherical approximation for the hard wall model led to estimates for $\Delta\sigma$ of a few tenths of an angström.

The purpose of this note is to propose an admittedly approximate method for estimating the magnitude of $\Delta\sigma$ by considering in some detail the microscopic structure of the metal electrode. However, since both the distribution of electrons spilling out from the planar metal electrode, and the microscopic ionic structure of the electrode, are involved, it is, of course, essential to work with a rather primitive model.

2 MODEL OF STRUCTURE OF METAL ELECTRODE

Here, we adopt the widely used Bardeen model,[2] in which the electronic wave functions representing the metal electrons are confined by an infinite barrier, placed outside the semi-infinite jellium neutralizing background at a distance $\xi = 3\pi/8k_{\mathrm{F}}$, where k_{F} is the Fermi wave number of the electron gas (cf. Figure 1).

The capacitance of this model electrode has been calculated by Newns,[3] with the result that the induced electronic charge has its centre of gravity at a distance

$$d_m \simeq k_{\mathrm{TF}}^{-1} + \pi/(4k_F) \tag{2.1}$$

from the Bardeen infinite barrier. Here k_{TF}^{-} is the Thomas-Fermi screening length.

Of course, this discussion so far has not considered the granular nature of the metal ions in the electrode, of ionic radius R_c say, nor the size of the molten salt ions and their distance of closest approach to the metal surface. The question that must be addressed is where the pseudopotentials representing the granular metal ions are to be centred relative to the edge of the semi-infinite jellium background. Calling this distance $\frac{1}{2}d$, as shown in Figure 1, we expect from electrical neutrality that d will be approximately the near-neighbour distance in the metal, say d_n.

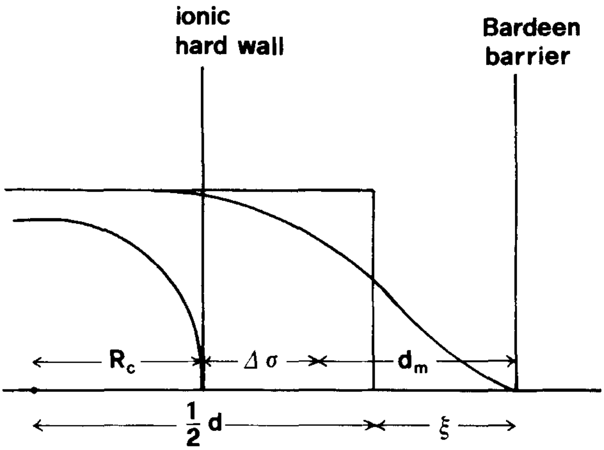

FIGURE 1 Schematic model of metal-molten salt interface. The semi-infinite jellium edge is at distance ξ from Bardeen infinite barrier. Spill-out electron density (omitting Friedel oscillations) from the metal electrode is depicted, and vanishes at Bardeen barrier. d_m denotes the screening length calculated by Newns.[3] The length $\Delta\sigma$ entering Eq. (1.2) is also shown, as is the metal ion core radius R_c. The centre of the metal ion is at distance $\frac{1}{2}d$ from the jellium edge. The hard wall for the molten salt ions is taken at the metal ion core radius, as shown in the Figure.

We place next the 'hard wall' for the molten salt ions at distance R_c from the metal ion centres as shown again in Figure 1. At this point, we note further that, provided the molten salt ions have ionic radii $\frac{1}{2}\sigma_+$ and $\frac{1}{2}\sigma_-$ such that $R_i = \frac{1}{2}(\sigma_+ + \sigma_-)$ is greater than the distance separating the hard wall for the ions from the Bardeen barrier, then the method of Newns can still be applied to describe the contribution of the metal electrode to the interface capacitance. On the other hand, if this condition is violated, the electrostatic arguments are incomplete.

Assuming that the above condition is satisfied, then the interface capacitance is given by Eq. (1.2), with $\Delta\sigma$ (see Figure 1) given by

$$\Delta\sigma = \xi + \tfrac{1}{2}d - R_c - d_m. \tag{2.2}$$

The length $\Delta\sigma$ will be a positive quantity if, as depicted in Figure 1, the hard wall lies behind the centre of gravity of the displaced electronic charge. This was found necessary in Ref. 1 in order to establish contact between Eq. (1.2) and experimental values of the capacitance for a Pb electrode at the point of zero charge.

It remains to estimate $\Delta\sigma$ from Eq. (2.2). Data is available for several molten salts with a liquid Pb electrode.[4] For this electrode, and also for a Hg electrode, Table I gives values of the relevant metal parameters. The

TABLE I

Relevant metal parameters calculated for Pb and for Hg electrodes

	Pb^{4+}	Hg^{2+}
k_F (Å^{-1})	1.57	1.36
ξ (Å)	0.75	0.87
d_m (Å)	1.01	1.13
d_n (Å)	3.49	3.00
R_c (Å)	0.84	1.12
$\xi + \frac{1}{2}d_n - R_c$ (Å)	1.66	1.25
$\Delta\sigma$ (Å)	0.65	0.12

only comment we need make on the data there is that the values of R_c were taken as Goldschmidt ionic radii.

As to the results in the last two rows of Table I, the values for the quantity $\xi + \frac{1}{2}d_n - R_c$ are comparable with the ionic length R_i.[5] This comparison makes clear that while there is a degree of overlap between the spill-out electron cloud from the electrode and the molten salt ions, it does not seriously invalidate the electrostatic arguments. The length $\Delta\sigma$ appearing in Eq. (1.2) is seen to vary substantially between Pb and Hg electrodes, but to have the order of magnitude established in Ref. 1.

Relating to the magnitude, and most importantly the sign of $\Delta\sigma$ in Eq. (1.2), it could be argued that there are significant differences between the Bardeen model we have used and more refined treatments of the jellium surface, e.g. Lang and Kohn; see e.g. Lang's review in Ref. 6. One such difference is that the centre of gravity of the displaced electronic charge under a weak external field would be moved outside the semiinfinite jellium edge. To connect with Figure 1, this could be thought of as equivalent to a decrease in the distance d_m. Though this would change substantially the quantitative values of $\Delta\sigma$, it would reinforce our main point that $\Delta\sigma$ in Eq. (1.2) is positive and of the order of several tenths of an Å.

3 CONCLUDING REMARKS

It should be mentioned here that quantitative work on a density functional treatment of electron spill-out from the metal electrode has been reported by Schmickler and Henderson[7–9] in connection with aqueous electrolyte solutions, not molten salts. Their results and ours appear to be consistently predicting a location of the centre of gravity of the displaced electronic charge lying in front of the hard wall encountered by the electrolyte.

The final point to be emphasized is that a full test of the Eq. (2.2) presented here for $\Delta\sigma$ will require, from Eq. (1.2), knowledge of the screening length l_s in Eq. (1.1) for the hard wall-molten salt interface. Other statistical mechanical methods than the mean spherical approximation have been explored for this model.[10] Different theories lead to substantially different predictions for l_s which plainly lead to ambiguities in an empirical determination of $\Delta\sigma$. Therefore, we are currently doing Monte Carlo simulation of the hard wall-molten salt interface, in order to remove this ambiguity.

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