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A Model for the Surface of a Molten Salt

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A model is proposed for the two-particle distribution functions for the surface region of a system composed of two oppositely charged species with identical hard sphere repulsions. The distribution functions are formed from those for the bulk fluid by incorporating a cutoff corresponding to the surface and a multiplying factor defined so as to guarantee electroneutrality while maintaining the proper symmetry. Various methods for doing this are discussed. Good agreement is obtained for surface tension and surface energy. Density oscillations are predicted.

I. Introduction

We consider a system composed of two oppositely charged species, with the interaction potential between a particle of species $i$ and one of species $j$ given by a Coulombic potential, $e_i e_j/r_{ij}$, plus a hard sphere repulsion, the hard sphere radii being identical for positively and negatively charged species (restricted primitive model). This set of assumptions seems to give a good description of molten salts and other ionic systems. By a model for the particle of species $i$ and one of species $j$ given by a Coulombic potential, we mean a formula for the two-particle distribution functions $\rho_{ij}(\vec{r}_1, \vec{r}_2)$, where $\delta^{(3)}(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2$ gives the average number of pairs of particles of species $i$ and $j$, such that a particle of species $i$ is found in a volume $d^3r_1$ at $\vec{r}_1$ and a particle of species $j$ in a volume $d^3r_2$ at $\vec{r}_2$. From $\rho_{ij}(\vec{r}_1, \vec{r}_2)$ one can obtain $\nabla \cdot \rho_{ij}(\vec{r}_1)$, where $\rho_{ij}$ is the one-particle distribution function or density for species $i$, by the Born–Yvon–Green equation.

To describe a surface region, the Fowler–Kirkwood–Buff or superposition approximation is often used. This approximation makes $\rho_{ij}(\vec{r}_1, \vec{r}_2)$ identical with the corresponding distribution function of the bulk fluid as long as $\vec{r}_1$ and $\vec{r}_2$ are both within the liquid region, and zero if either is outside:

$$\rho_{ij}(\vec{r}_1, \vec{r}_2) = \rho_{ij}^{\text{bulk}}(\vec{r}_1, \vec{r}_2) \{1 - \delta(z_1)[1 - \delta(z_2)]\}$$  \hspace{1cm} (1)

Here $z$ gives position on the direction normal to the surface, and $\delta(z_1)$ is the step function, equal to 1 for $z_1 > 0$ and 0 for $z_1 < 0$. The bulk distribution function depends only on $\vec{r}_{ij}$, reflecting the isotropy and homogeneity of the fluid. For the surface region, $\rho_{ij}^{(3)}$ may depend on $z_1$ and the components of $\vec{r}_{ij}$. Conventionally, one includes in the Fowler approximation a step-function formula for the one-particle distribution functions. However, the assumption for $\rho_{ij}^{(3)}$ is inconsistent with that for $\rho_{ij}^{(2)}$, as appears from the large and nonconstant normal pressure calculated using both assumptions. If $\rho_{ij}^{(3)}$ is derived from $\rho_{ij}^{(2)}$ using the Born–Yvon–Green equation, the calculated normal pressure is constant, as it should be.

From the $\rho_{ij}^{(2)}$ one can calculate the surface tension $\gamma$ and surface energy $E_s$. When the generalized mean spherical approximation is used to obtain $\rho_{ij}^{\text{bulk}}$, the results for $\gamma$ and $E_s$ for NaCl at 1128 K (see Table I) are so far from the experimental values as to indicate a serious problem with the approximation (1) for $\rho_{ij}^{(2)}$, a problem which apparently is not present for one-component systems for which this model has been used. Use of a better interaction potential and $\rho_{ij}^{\text{bulk}}$ from Monte Carlo calculations does not improve the situation.

### Table I: Calculated Surface Properties of NaCl ($T = 1128$ K)

| Source | Surface Tension $\gamma$, dyn/cm | Surface Energy $E_s$, dyn/cm |
|--------|----------------------------------|-----------------------------|
| Fowler model (superposition) previous model (eq 6) | 99.36 | 288.08 |
| present model (eq 9) | 111.3 | 216.2 |
| experimental | 90.75 | 207.8 |

* G. Janz, “Molten Salts Handbook”, Academic Press, New York, N.Y., 1967. Calculated from $\gamma = \gamma' + \int d\gamma/ dt$ from ref a.

Of the difficulty seems to lie in the violation of the electroneutrality condition.

This is best expressed by writing

$$\rho_{ij}^{\text{bulk}} = \rho_{ij}^{\text{bulk}}\rho_{ij}^{\text{bulk}}g_{ij}(z_{12})$$

where $\rho_{ij}^{\text{bulk}} = \rho_{ij}^{\text{bulk}}$ is the one-particle density of species $i$ and defining

$$g^0(z_{12}) = g^0_+(z_+ + z_+)$$

$$g^0(z_{12}) = g^0_+(z_+ + z_+)$$

$$g^0(z_{12}) = g^0_-(z_+ + z_-)$$

Of course, $g_+ = g_+$ and $g_- = g_-$ in this model. With the assumptions of our model (eq 1) the total charge around a positive ion at $\vec{r}_1(z_1 < 0)$ is

$$(\rho/2)^{-1} \int d\tau_2 e^{(\rho_{+}^{(2)}(\vec{r}_1, \vec{r}_2) - \rho_{-}^{(2)}(\vec{r}_1, \vec{r}_2))} = -\rho e \int (rt) d\tau_2 g^D(z_{12})$$

where $e = e_+ + e_-$. It should equal $-e$, but, working out the integral in detail, we find

$$(\rho/2)^{-1} \int d\tau_2 e^{(\rho_{+}^{(2)} - \rho_{-}^{(2)})} = -4\pi e \left[ \int_0^{z_1} r^2 dr g^D(r) + \int_0^{z_2} r^2 dr g^D(r)(-1 + z_2 r) \right]$$

(5)

Since the bulk correlation function satisfies $\int g^D(r) dr = 1/4\pi$, we have electroneutrality when $z_2$ is large, but not otherwise. The right side of (5) is plotted as a function of $z_1$ in Figure 1A. Henceforth, we shall represent the combination of correlation functions given in (3b) by $g^D$ when the functions $g_+$ and $g_-$ are taken from bulk calculations without modification, and use $g^D$ for the
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According to a positive ion at curve B, using eq 8 for $g^D$, curve C, using eq 10 with $f$ calculated according to eq 7.

The corresponding function for the surface; $g^D$ depends on $z_1$, $z_2$, and $\varphi_{12}$. In our previous work; we corrected the problem by writing

$$g^D = f(z_1) \cdot g^B(r_{12})$$

where

$$f(z_1) = (4\pi \rho)^{-1} \left[ \int_0^{\varphi} \varphi^2 \, d\varphi \left[ g^B(r) + \frac{1}{2} \int_{\varphi_1}^{\varphi} \varphi^2 \, d\varphi \right] \right]^{-1}$$

and leaving $g^B$ unchanged. This makes (5) exactly equal to $-e$. Much improved values for surface tension and surface energy were obtained (see Table I). We pointed out, however, that a symmetry condition was violated. We should have

$$g^D(z_1z_2s_{12}) = g^B(z_1z_2s_{12})$$

where $s_{12}^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2$, and this does not hold if $g^D$ of eq 6 is used. The present paper is concerned with correcting for electroneutrality while maintaining this symmetry.

II. A Model Satisfying the Symmetry Condition

One reasonable way of obtaining a symmetrical $g$ from the above choice is to write

$$g^D(z_1z_2s_{12}) = [f(z_1) f(z_2)]^{1/2} g^B(r_{12})$$

using eq 7 for $f$. The resultant $g^D$ is better than $g^B$ in assuring electroneutrality for small $z_1$, as shown in Figure 1B. However, it is not an improvement elsewhere. Another method was suggested by us: one could put $g^D = f(z_1) f(z_2) g^B(r_{12})$ and determine $f$ by solving the integral equation (see eq 4)

$$f(z_1) \int_0^{(\varphi_{z_{10}})} \, d\varphi \int_0^{(\varphi_{z_{20}})} \, d\varphi \, g^B(r_{12})$$

by an iterative method. Putting $f_1(z_2) = 1$, this gives for $f_1(z_1)$, the first approximation for $f(z_1)$, just eq 7. Attempts to implement this procedure were unsuccessful: we were unable to get convergence to a reasonable $f(z_1)$. Another solution to the symmetrization problem is to put $g^D = [f(z_1) + f(z_2)] g^B(r_{12})$, leading to

$$f_1(z_1) \int_0^{(\varphi_{z_{10}})} \, d\varphi \int_0^{(\varphi_{z_{20}})} \, d\varphi \, g^B(r_{12}) + \int_0^{(\varphi_{z_{10}})} \, d\varphi \int_0^{(\varphi_{z_{20}})} \, d\varphi \, g^B(r_{12})$$

In this case, the integral equation is linear, but the iterative procedure again failed to converge.

If it is assumed that $f(z) = 1/2$ (the asymptotic value) for $z < z_{10}$, eq 9 becomes a Fredholm's equation of the second kind, for which an exact method of solution is known. We solved this equation for several choices of $z_0$.

In Figure 1. Electron neutrality for various models of $g^D$: net charge around a positive ion at $z_2$, in units of $-e$: curve A, unmodified Fowler model; curve B, using eq 8 for $g^D$; curve C, using eq 10 with $f$ calculated according to eq 7.
As we have noted, our model of the interface is a model for the two-particle distribution functions \( \rho_{++}^{(2)} = \rho_{-}^{(2)} \) and \( \rho_{-}^{(2)} (\text{or} \rho_{-}^{(2)}) \), or alternatively, their sum and difference \( \rho^p \) and \( \rho^b \) (see eq 2 and 3). We use the bulk-fluid distribution function for \( \rho^b \), as in eq 1, and modify the bulk-fluid function for \( \rho^p \). The one-particle distribution functions \( \rho_1^{(1)} \) are to be computed from the Born–Green–Yvon equation:

\[
\frac{d\rho_1^{(1)}}{dz_1} = \frac{1}{kT} \sum \int dr_{12} u_g^2 (r_{12}^{-1} f(z_1) - f(z_2)) (r_{12}^{1/2} f(z_1)) \tag{12}
\]

Integrating (12) over all values of \( z_1 \) and noting that \( \rho_{+}^{(2)} = 0 \) for \( z_1 > 0 \), we obtain the difference between \( \phi_0 \) and \( \phi_{+}^{(2)} \), which should be just the negative of the density of the anion or cation in the bulk fluid. As shown in our previous work, use of the Fowler approximation (eq 1) gives the correct value, \( \rho/2 \), for this quantity, but, when we modify the distribution functions by multiplying \( \rho^b \) by \( f(z_1) \), this no longer holds true.

This deficiency in the previous model is remedied when the modification (9), which restores the symmetry of \( \rho^b \), is used. The effect of the correction is to add the following term to the integral of \( d\rho_1^{(1)}/dz_1 \):

\[
\frac{1}{kT} \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \int_{-\infty}^{\infty} s_{12} ds_{12} \times \int_{0}^{2\pi} \phi_0^2 \frac{e^{z_1}}{r_{12}^{1/2} r_{12}} (\rho_{--}^{(2)} - \rho_{++}^{(2)}) =

4\pi e^2 \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \int_{-\infty}^{0} s_{12} ds_{12} \frac{21}{r_{12}^{1/2}} [f(u) - 1] g_B^2 (r_{12}) \left( \frac{\rho}{2} \right)^2 \tag{13}
\]

The value of \( L \) will eventually be allowed to become infinite; \( u = 1/s_{12} + 2z_1 \). Now let \( x = z_2 - z_1 = z_{12} \), and write

\[
\int_{-\infty}^{0} s_{12} ds_{12} r_{12}^{-2} g_B^2 (r_{12}) = \int_{-\infty}^{\infty} s_{12} ds_{12} f(u) - 1 + G^{(2i)}(x) \tag{14}
\]

where \( G^{(2i)}(y) \) is the \( i \)th moment of \( g^b \) from \( y \) to \( -\infty \), which we have previously tabulated. Equation 13 becomes

\[
\frac{\pi e^2}{kT} \int \int dz_1 \int dx x [f(u) - 1] G^{(2i)}(x) = \frac{\pi e^2}{kT} \int \int dz_1 \int dx x G^{(2i)}(x) + \int \int dz_1 \int dx x [f(u) - 1] G^{(2i)}(x) \tag{15}
\]

In the first term, the integral over \( x \) vanishes because the integrand is odd; if \( L \) is large enough (7.2 hard sphere diameters in the present case) so that \( f(u) = 1 \) for \( u < -L \), the second term also vanishes.

For calculation of \( d\rho_1^{(1)}/dz_1 \), at a particular value of \( z_1 \), the contribution additional to the Fowler contribution is obtained according to (see eq 13 and 14):

\[
\frac{d\rho_1^{(1)}}{dz_1} = \frac{\pi e^2}{kT} \int dx x [f(u) - 1] G^{(2i)}(x) = \frac{\pi e^2}{kT} \int dx x [f(z_1 + 1/2z_{12}) - 1] G^{(2i)}(x) \tag{16}
\]

Here, \( x_0 = -14.4 \sigma - 2z_1 \). The results of this calculation are given in Figure 3. The density gradient \( d\rho_1^{(1)}/dz_1 \), from the unmodified Fowler–Kirkwood–Buff model is plotted as well as \( d\rho_1^{(1)}/dz_1 \) from our model (Fowler–Kirkwood–Buff results plus correction of eq 15). It is clear that our modification leads to more pronounced oscillations, extending further into the bulk. With the step function of \( \rho_1^{(1)} \) (eq 1), \( d\rho/du \), vanishes for \( z_1 > 0 \), while Figure 3 shows that it has its largest magnitude for \( z_1 \) just below zero. We conclude that satisfaction of the electroneutrality constraint, which could provide a reasonable description of the interface, is untenable for this system, into one which could provide a reasonable description of the interface. What one requires now are additional constraints...
enabling us to further refine the model (only $g^D$ and not $g^E$ (eq 3 and 4) has been altered), or further data for testing the predictions of the model. In particular, there is the fact that the improvement in calculated properties between the Fowler–Kirkwood–Buff and the present model is accompanied by a large increase in the oscillations in the one-particle distribution function or density.

One thermodynamic property which should be satisfied by the statistical mechanical model for the interface is the Gibbs–Helmholtz equation

$$E^\beta = \gamma - T(\frac{\partial \gamma}{\partial T})$$

Verifying this equation is difficult; furthermore, it is likely that the sharp cutoffs in $\rho_{ij}$ (eq 1) become worse approximations as the temperature increases. The fact that $E^\beta$ agrees much less well with experiment than $\gamma$ may be taken as an indication that the Gibbs–Helmholtz equation is not satisfied. Another property is expressed by the Gibbs–Lippmann equation

$$\left(\frac{\partial E}{\partial \rho}\right)_T = -q$$

where $E^\beta$ is the drop in electrical potential across the interface and $q$ the electrical charge per unit area of the surface double layer.10 The present model of course has neither double layer nor potential drop. Modification of the assumptions, to produce asymmetries between anions and cations, would be interesting to study.

**Supplementary Material Available:** Table II, giving the function $f$ which guarantees electroneutrality (3 pages). Ordering information is available on any current masthead page.

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**Spectroscopy of Polynes. 1. Comprehensive Investigation of Absorption Spectra of Polyenals and Polyenones Related to Visual Chromophores**

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The absorption spectra of various homologues and analogues of retinals, a total of 21, with varying number of double bonds ($n$) have been examined in detail under various conditions of solvent and temperature. Altogether six band systems have been identified and their oscillator strengths and transition energies are presented as functions of chain length. The origin of the transitions is discussed in the light of the results of semiempirical calculations available in the literature. The trend in the lower polyene systems ($n = 2-4$) where the $3(n,\pi^*)$ state is seen in absorption clearly indicates that this latter state is the lowest singlet state in these systems, and is close to the $B_s$ state in retinals and their analogues. The $\sim 280$-nm band system in retinals and their analogues, heretofore not satisfactorily assigned, is traceable to a more intense band in the lower homologues and is tentatively interpreted in terms of absorption of 6-s-trans conformers present in solution to the extent of $\sim 10\%$ in equilibrium with distorted 6-s-cis conformers. The absorption spectra of retinones and C16 ketones indicate methyl–methyl and methyl–hydrogen steric interaction leading to geometric distortion of the polyene chain.

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**I. Introduction**

In recent years, a great deal of theoretical and experimental work has been done on retinals and related polyene systems.1-4 However, a number of questions and controversies regarding the spectral properties of these systems still remain unresolved. Some of these concern the relative order of the three low-lying singlet states, $1A_s^+$, $1B_u^+$, and $1(n,\pi^*)$,5-10 the nature of the lowermost singlet state,11-22 the location of the cis band ($1A_g^+ \rightarrow 1A_g$ transition),23,24 the assignment of the 280–300-nm band system (in retinals),25,26,27,28 and the absorption spectral analogue of 11-cis-retinal.29,30

In the present investigation, we have studied 21 polyenals and polyenones that are related to retinals as analogues and homologues. The low-lying excited states of photophysical and photochemical interest in many of these systems are expected to be comparatively sparsely located and to provide situations with relative state order different from that in retinals. Although there have been a few early spectroscopic studies20-22 on some of the polyene systems under examination, these were concerned with room temperature spectra and limited to band maxima (as routine work in the course of synthesis). No detailed systematic analysis has ever been undertaken with the object of understanding the existent problems concerning retinals, their homologues, and visual pigments.

In paper 1, we propose to present the absorption spectral data and attempt to interpret them in the light of the results of theoretical calculations available to date. In paper 2, we shall report the data on fluorescence, quantum