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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, $e_{ij}/r_{ij}$, 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 charged species, with the interaction potential between a hard sphere radius being identical for positively and negatively charged species, we mean a formula for the two-particle set of assumptions seems to give a good description of molten salts and other ionic systems. By a model for the two-particle interaction potential and $g_{ij}$ 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 $dV_i$ at $r_i$ and a particle of species $j$ in a volume $dV_j$ at $r_j$.

To describe a surface region, the Fowler–Kirkwood–Buff or superposition approximation is often used. This approximation makes $\rho_i^{(2)}(r_i,r_j)$ identical with the corresponding distribution function of the bulk fluid as long as $r_i$ and $r_j$ are both within the liquid region, and zero if either is outside:

$$\rho_i^{(2)}(r_i,r_j) = \rho_i^{\text{bulk}}(r_i,r_j)[1 - \theta(z_i)][1 - \theta(z_j)]$$

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

From the $\rho_i^{(2)}$ one can calculate the surface tension $\gamma$ and surface energy $E_s$. The calculated normal pressure of spherical approximation is used to obtain $\rho_i^{\text{bulk}}$, the results for $\gamma$ and $E_s$ for NaCl at 1128 K (see Table I) are so far from the experimental values that a modification of the measurement, in which both the distribution $g_{ij}$ and $g_{ij}$ are taken from bulk correlation functions over the surface region, is 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.

| TABLE I: Calculated Surface Properties of NaCl ($T = 1128$ K) |
|------------------|------------------|
| source           | surface tension $\gamma$, dyn/cm | surface energy $E^s$, dyn/cm |
| Fowler model     | -79.58           | 907.52 |
| (superposition)  |                  |      |
| previous model   | 42.37            | 111.87 |
| present model    | 99.36            | 288.08 |
| experimental     | 111.3            | 216.2  |

Of course, $g_{ij} = g_{ij}$ and $g_{++} = g_{ij}$ in this model. With the assumptions of our model (eq 1) the total charge around a positive ion at $r_1(z_1 < 0)$ is

$$\rho^{(1)} = \frac{1}{2} \int d^3r_2 \, e(\rho_{++}^{(2)}(r_1,r_2) - \rho_{--}^{(2)}(r_1,r_2)) = -\rho \int dr_2 \, g^D(r_2)$$

where $\rho = \rho_+^{\text{bulk}} + \rho_-^{\text{bulk}}$. It should equal $-e$, but, working out the integral in detail, we find

$$\rho^{(1)} = \frac{1}{2} \int d^3r_2 \, e(\rho_{++}^{(2)}(r_1,r_2) - \rho_{--}^{(2)}(r_1,r_2)) = -\rho \int dr_2 \, g^D(r_2)$$

Since the bulk correlation function satisfies $\int \rho \int d^3r \, g^D(r) = 1/(4\pi \rho)$, we have electroneutrality when $|z_1|$ is large, but not otherwise. The right side of (5) is plotted as a function of $z_1$ in Figure 1A. Therefore, for the combination of correlation functions given in (3b) by $g^B$ when the functions $g_{ij}$ and $g_{ij}$ are taken from bulk calculations without modification, and use $g^D$ for the
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corresponding function for the surface; \( g^D \) depends on \( z_1 \), \( z_2 \), and \( f(z_2) \).

In our previous work, we corrected the problem by writing

\[
g^D = f(z_1) \, g^B(r_{12})
\]

where

\[
f(z_1) = (4\pi\rho)^{-1} \left[ \int_0^{r_2^2} \, r \, g^B(r) \, dr \right] + \frac{1}{2} \left[ \int_0^{r_2^2} \, r \, g^B(r)(-1 + |z_1|^2)^{-1} \right]^{-1}
\]

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

\[
g^B(z_1, z_2, s_{12}) = g^B(z_2, z_1, s_{12})
\]

where \( s_{12}^2 = (z_1 - z_2)^2 + (y_1 - y_2)^2 \); 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

\[
g^D(z_1, z_2, s_{12}) = [f(z_1) \, f(z_2)]^{1/2} \, g^B(r_{12})
\]

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 \( g^D = f(z_1) \, g^B(r_{12}) \) and determine \( f \) by solving the integral equation (see eq 4)

\[
\rho^{-1} = f(z_1) \int (x < 0) \, dr_2 \, f(z_2) \, g^B(r_{12})
\]

by an iterative method. Putting \( f(z_2) = 1 \), this gives for \( f(z_1) \), 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

\[
\rho^{-1} = f(z_1) \int (x < 0) \, dr_2 \, g^B(r_{12}) + \int (x < 0) \, dr_2 \, f(z_2) \, g^B(r_{12})
\]

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

If it is assumed that \( f(c) = 1/2 \) (the asymptotic value) for \( z < z_0 \); 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 \( z_0 \).
As we have noted, our model of the interface is a model for the two-particle distribution functions \( \rho_{+}^{(2)} = \rho_{-}^{(2)} \) and \( \rho_{+}^{(2)} = \rho_{-}^{(2)} \), or, alternatively, their sum and difference \( \rho_{+}^{(2)} \) and \( \rho_{-}^{(2)} \) (see eq 2 and 3). We use the bulk-fluid distribution function for \( \rho_{+}^{(2)} \) as in eq 1, and modify the bulk-fluid function for \( \rho_{-}^{(2)} \). The one-particle distribution functions \( \rho_{+}^{(1)} \) are to be computed from the Born–Green–Yvon equation:

\[
\frac{d\rho_{+}^{(1)}}{dz_1} = \frac{1}{kT} \sum_{z_2} \int d\tau_{12} u_{ij}(\tau_{12}) \frac{z_{12}}{r_{12}} (r_{12})_{z_1} (z_1)_{z_2} \tag{12}
\]

Integrating (12) over all values of \( z_1 \) and noting that \( \rho_{+}^{(2)} = 0 \) for \( z_1 > 0 \), we obtain the difference between \( \rho_{+}^{(0)} \) and \( \rho_{+}^{(-)} \), 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 \( \rho_{-}^{(2)} \) by \( f(z_2) \), this no longer holds true.

This deficiency in the previous model is remedied when the modification (9), which restores the symmetry of \( \rho_{-}^{(2)} \), is used. The effect of the correction is to add the following term to the integral of \( d\rho_{+}^{(1)}/dz_1 \):

\[
\int_{-\infty}^{z_1} d\tau_{12} s_{12} (G_{1}(\tau_{12}) = \int_{|z|}^{z_1} r_{12} s_{12} (G_{1}(\tau_{12})) = G_{0}^{(+)}(\{x\}) \tag{13}
\]

where \( G_{0}^{(+)}(\{x\}) \) is the \( i \)th moment of \( g_{ij}^{(2)} \) from \( x \) to \( \infty \), which we have previously tabulated. Equation 13 becomes

\[
\frac{\pi \rho_{-}^{(2)}}{kT} \int_{-\infty}^{z_1} dx \int_{-\infty}^{z_1} dx x[f(u) - 1] G_{1}^{(-)}(\{x\}) = \frac{\pi \rho_{-}^{(2)}}{kT} \int_{-\infty}^{z_1} dx \int_{-\infty}^{z_1} dx x G_{1}^{(-)}(\{x\}) + \int_{-\infty}^{z_1} dx \int_{-\infty}^{z_1} dx x \int_{-\infty}^{z_1} dx x G_{1}^{(-)}(\{x\}) \tag{14}
\]

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

\[
\frac{d\rho_{+}^{(1)}}{dz_1} = \frac{\pi \rho_{-}^{(2)}}{kT} \int_{-\infty}^{z_1} dx \int_{-\infty}^{z_1} dx x[f(u) - 1] G_{1}^{(-)}(\{x\}) = \frac{\pi \rho_{-}^{(2)}}{kT} \int_{-\infty}^{z_1} dx \int_{-\infty}^{z_1} dx x[f(z_1 + \frac{1}{2}z_2) - 1] G_{1}^{(-)}(\{x\}) \tag{15}
\]

Here, \( z_2 = -14.4 \sigma - 2z_1 \). The results of this calculation are given in Figure 3. The density gradient \( d\rho_{+}^{(1)}/dz_1 \) from the unmodified Fowler–Kirkwood–Buff model is plotted as well as \( d\rho_{+}^{(1)}/dz_1 \) 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 \( \rho_{+}^{(2)} \) (eq 1), \( d\rho_{+}^{(2)}/dz_1 \) vanishes for \( z_1 > 0 \), while Figure 3 shows that it has its largest magnitude for \( z_1 \) just below zero. The discontinuity in \( d\rho_{+}^{(2)}/dz_1 \) could be removed by using a smooth function instead of \( 1 - \theta(z_1) \) in eq 1.

From \( d\rho_{+}^{(2)}/dz_1 \) one could compute the density profile, integrating inward from \( z_1 = 0 \). Clearly, our model predicts a density profile which has strong oscillations (\( \rho_{+}^{(2)}(\infty) \) is about 10\(^{12} \) cm\(^{-3} \)). This may imply that such oscillations really exist in this system: they do not seem to occur in surface systems studied. The enhanced oscillations represent the influence of the electroneutrality constraint, which is a reflection of the long-range character of the Coulombic force, not present in systems considered in the past. In this system, we find, furthermore, attractive forces and repulsive forces of the same range. This would seem to create the possibility that \( d\rho_{+}^{(2)}/dz_1 \) take both positive and negative values in the surface region.

Returning to the surface tension, we find, by treating (11) like (13), the following additional contribution:

\[
\gamma - \gamma_{F} = \frac{\pi \rho_{-}^{(2)}}{2} \int_{-\infty}^{z_1} dz_1 \int_{-\infty}^{z_1} dz_2 [f(u) - 1] \times \int_{-\infty}^{z_1} dz_1 \int_{-\infty}^{z_1} dz_2 [f(z_1 + \frac{1}{2}z_2) - 1] G_{0}^{(+)}(\{z_1\}) = \frac{\pi \rho_{-}^{(2)}}{2} \int_{-\infty}^{z_1} dz_1 \int_{-\infty}^{z_1} dz_2 [f(z_1 + \frac{1}{2}z_2) - 1] G_{1}^{(-)}(\{z_1\}) \tag{16}
\]

For the surface energy, we find

\[
E_{S} - E_{S,F} = \frac{\pi \rho_{-}^{(2)}}{2} \int_{-\infty}^{z_1} dx \int_{-\infty}^{z_1} dx x[f(z_1 + \frac{1}{2}z_2) - 1] G_{1}^{(-)}(\{z_1\}) \tag{17}
\]

where \( u = 1/2(z_1 + z_2) \), \( \alpha = 2(7.2 \sigma - z_1) \), and \( G_{0}^{(+)} \) defined by (14). Since the moments of \( g_{ij}^{(2)} \) have been previously calculated, a double integral over \( z_1 \) and \( z_2 \) is required to evaluate the additional contributions to \( \gamma \) and to \( E_{S} \). They are 178.94 and -619.45 dyn/cm, respectively. As shown in Table I, the total values for surface tension and surface energy are in reasonable agreement with experiment. As usual, the agreement is much better for the former.

We conclude that satisfaction of the electroneutrality and symmetry conditions on the two-particle distribution functions converts the Fowler–Kirkwood–Buff model of the surface region, untenable for this system, into one which could provide a reasonable description of the interface. What one requires now are additional constraints.
Spectroscopy of Polyenes

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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 \((n,\pi^*)\) 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 \(~280\)-nm band system in retinals and their analogues, heretofore not satisfactorily assigned, is traceable to a more intense band system in the lower homologues and is tentatively interpreted in terms of absorption of 6-s-trans conformers present in solution to the extent of \(~10\)% in equilibrium with distorted 6-s-cis conformers. The absorption spectra of retinones and \(C_{18}\) ketones indicate methyl-methylene and methyl-hydrogen steric interaction leading to geometric distortion of the polyene chain.

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, \(1\text{A}_{1}, 1\text{B}_{3}, \text{and} 1(n,\pi^*)\),\(^5\)–\(^10\) the nature of the lowest singlet state,\(^11\)–\(^14\) the location of the cis band (\(2\text{A}_{2}^* \rightarrow 1\text{A}_{2}\) transition),\(^14\)\(^6\)\(^7\)\(^8\)\(^9\)\(^15\) the assignment of the 280–300-nm band system (in retinals),\(^14\)\(^6\)\(^7\)\(^8\)\(^9\)\(^15\) and the absorption spectral analogue of 11-cis-retinal.\(^16\)\(^17\)

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 studies\(^18\)–\(^22\) 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

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References and Notes


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Supplementary Material Available: Table II, giving the function f which guarantees electroneutrality (3 pages).

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