applied to both sides of equation 138, this equation may be linearized with respect to $\varphi(r_{23})$ for *all* $\mathbf{r}_3$, and $g_m(r_{23})$ may be replaced by unity:

$$\nabla_1{}^2 \varphi(r_{12}, \lambda) = -\frac{\lambda \kappa^2}{4\pi} \nabla_1{}^2 \int d^3\mathbf{r}_3 \, \frac{g(r_{13}, \lambda)}{r_{13}} \, \varphi(r_{23})$$

$$\kappa^2 = \frac{8\pi c (ze)^2}{DkT}, \qquad (r_{12} \text{ large}) \tag{140}$$

On account of the demand that r_{12} be large in derivation of the linear and homogeneous integrodifferential equation (eq. 140), this cannot be the proper form of an equation satisfied by φ when r_{12} is small. Nevertheless, there will exist some function $h(r_{12}, \lambda)/r_{12}$ which may be added to the right-hand side of equation 140 which will convert it into a relation satisfied exactly by φ for *all* r_{12}:

$$\nabla_1{}^2 \varphi(r_{12}, \lambda) = \frac{h(r_{12}, \lambda)}{r_{12}} - \frac{\lambda \kappa^2}{4\pi} \nabla_1{}^2 \int d^3\mathbf{r}_3 \, \frac{g(r_{13}, \lambda)}{r_{13}} \, \varphi(r_{23}) \tag{141}$$

An explicit form for this inhomogeneous function may be immediately obtained by comparison of this last equation with the nonlinear equation 138. Its most important characteristic for present purposes is simply that it decays to zero with increasing r_{12} sufficiently fast that only the homogeneous equation 140 remains at large r_{12}.

When λ is set equal to $+1$, utilization of a one-dimensional Fourier transform on equation 141 leads to a solution for $\varphi(r_{12})$ as the integral (68):

$$\varphi(r_{12}) = \frac{1}{2\pi r_{12}} \int_{-\infty}^{+\infty} \frac{2i\chi z - H(z)}{z^2 + {}^1\!/_2 \kappa^2 j(z)} \exp\,(-i r_{12} z) dz$$

$$H(z) = 2 \int_0^\infty h(r_{12}) \sin\,(z r_{12}) dr_{12} \tag{142}$$

$$j(z) = 2 + 2z \int_0^\infty [g(r_{12}) - 1] \sin\,(z r_{12}) dr_{12}$$

The constant χ is arbitrary insofar as the first of these last equations represents a solution to integrodifferential equation 141. Its value, however, must be selected ultimately to satisfy the local electroneutrality condition, which in the present circumstances takes the form:

$$\frac{1}{8\pi c} = \int_0^\infty r^2 g_m(r) \tanh\left[\frac{\varphi(r)}{kT}\right] dr \tag{143}$$

this is analogous to the corresponding lattice theory relation, equation 114.

The contour of integration in equation 142 is along the real axis of the z plane except at poles of the integrand on the real axis. Whatever choice is ultimately adopted for the contour at these singularities, we may close the contour along the infinite semicircle in the lower half z plane (as indicated in Fig. 11), without changing the integral's value. Subsequently, the calculus of residues (71) may be used to express φ as an exponential series:

$$\varphi(r_{12}) = \frac{1}{r_{12}} \sum_k B_k \exp(-iz_k r_{12})$$

$$B_k = i \lim_{z \to z_k} \left[(z - z_k) \frac{2i\chi z - H(z)}{z^2 + {}^1\!/_2 \kappa^2 j(z)} \right] \tag{144}$$

The complex constants z_k are the poles of the integrand, for the first integral in equation 142, which lie within the closed contour.*

For z_k's which lie below the real axis, and therefore have negative imaginary parts, the corresponding term in φ damps exponentially to zero as r_{12} increases. But a z_k on the real axis will give rise to no such exponential damping, and the ion pair correlation functions obtained from such a φ would indicate order in the liquid at very large distances of pair separation. Wojtowicz (72) has shown that if such terms are retained in the sum for φ (eq. 144), then subsequent computation of the molten salt x-ray scattering pattern by equation 53 will predict strong Bragg-like reflections at certain angles, such as crystalline solids exhibit. Since the scattering patterns of molten salts are normal, however, in that the scattered radiation is much more diffusely distributed than from crystalline solids (see chapter by H. A. Levy), these non-exponentially damped contributions to φ should not be present. They may be eliminated by the simple expedient of deforming the integration path below each real singularity of the integrand as shown in Figure 11.† Therefore, since the

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* It has tacitly been assumed that all the poles are simple, but accidental multiplicity can occur for certain isolated values of the relevant physical parameters, (temperature, density). In this event, expression 144 for B_k must be modified in the usual way to yield the residue at this higher order pole.

† It is by analogy with this prescription that the lattice theory integral contour in equation 120 could be specified with similar deformation.
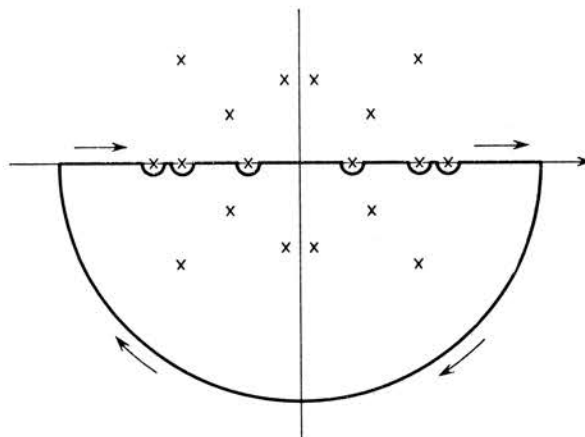
Fig. 11. Integration path in the inversion integral (eq. 142) for φ in the complete pair correlation function theory. The path is closed along the lower infinite semicircle. Crosses indicate the integrand's singularities. It should be noted that the contour must be deformed below several singularities on the real axis outside the range of integration of the cell theory integral for $\bar{\varphi}$ (Fig. 10).

resulting $\varphi(r_{12})$ decays exponentially to zero as r_{12} increases, the molten salt will exhibit electrostatically induced order for ion pairs only at moderate relative distances, which is in contrast with the long-range order covering the entire sample in the crystalline solid.

It was characteristic of the spatially coarse-grained lattice theory that the integral expression for $\bar{\varphi}$, in comparison with that for φ in the present analysis, had a finite integration interval which encountered only a pair of singularities. On the other hand, expression 142 for φ entails integration from minus to plus infinity, and the number of singularities below which deformation must occur is considerably larger (72), as indicated in Figure 11.

Detailed numerical calculations by the procedure outlined here have not yet been performed for the basic quantity φ. Such a program, however, does seem to be within the range of modern electronic computing facilities. To initiate such computations, it would be necessary to use pair correlation functions for fluids interacting with just the ion core potential, $V_N^{(s)}$. There are available such pair correlation functions for both rigid spheres (43) and for Lennard-Jones 12-6 particles (14), which should be valuable in this connection.

The remaining terms in the φ sum (eq. 144) combine to produce a real function of r_{12} which, aside from the r_{12}^{-1} factor, is a sum of exponentially damped sinusoids. In view of this fact, and also in analogy with the closely allied lattice theory, one is led anew to picture the molten salt as possessing alternate shells of ions about a given ion, which alternate in sign of charge, but lose distinctiveness rapidly as distance increases from the central ion. Since true crystals retain sharply defined shells of neighbors at all distances, this loss of order appears to be characteristic of liquids.

It has previously been remarked that the lattice theory automatically reduces to a correct Debye-Hückel limiting description for fluid electrolytes when κ is very small. It may likewise be shown on very general grounds (68) that equation 144 for φ also reproduces this result. It is the potential power and generality of the pair correlation function theory outlined in this section that it may comprehensively describe the full transition from the Debye-Hückel regime (where ion charge atmospheres have the simple monotonic decay form) to the normal molten salts, with ions shielded by concentric shells of charge of alternating sign.

In order to evaluate the molten salt chemical potentials, by formula 50, it is necessary to have available the $g^{(2)}$'s over the entire range $0 \leq \lambda \leq 1$. Once φ has been obtained for $\lambda = 1$, as represented by equation 144, this result may be inserted under the integral of the nonlinear equation 138 to yield the full λ dependence of φ.

We shall close this section on prediction of fused salt pair correlation functions with a few comments concerning generalization of the procedure to salts with ions having unlike short-range pair forces. It has been pointed out (68) that for ions which do not differ drastically in size, it is almost exclusively opposite types of ions which come close enough into contact for the details of core forces to matter; the electrostatic repulsions between two ions of the same type make close encounters a rare event. This surmise is supported by observation of vestigial solid-like ordering for the elementary class of salts, with the nearest neighboring shell composed of ions of the type opposite the central ion. As a result, the properties of the salt appear to depend almost exclusively on the short-range force law between unlike, rather than like, pairs, and so assumption that all short-range interactions are of the former type should commit little error. The statistical mechanical problem then

would amount to just that for the ideal class of salts considered above in detail.*

On the other hand, salts possessing an extreme ion size ratio, such as LiI, seem to require a considerable elaboration of the computational scheme. In this case, the larger ions can easily be "in contact" with their own kind, the smaller ions simply fitting into the interstices. The use of a common core force then is entirely inappropriate. One no longer has appeal to the simplification of equality of $g_{++}^{(2)}$ and $g_{--}^{(2)}$, so there are three independent pair correlation functions to be determined, rather than just two, as in the charge-symmetric model for the simple class of salts. Furthermore, the average of a like and an unlike pair correlation function, used to define g_m in equation 123, will no longer suffice to cause cancellation of the electrostatic correlations at moderate and large distances.

The case of an unsymmetrical electrolyte, for any ion core short-range forces, is similarly complicated by independence of $g_{++}^{(2)}$, $g_{+-}^{(2)}$, $g_{--}^{(2)}$. This likewise requires generalization of the foregoing procedure.

If the large r fluctuations of each of $g_{++}^{(2)}$, $g_{+-}^{(2)}$, and $g_{--}^{(2)}$ in the general fused salt are characterized by essentially the *same* damped sinusoid (though with arbitrary phase and amplitude), then there will exist constants A and B such that if

$$g_m(r) = \frac{1}{A + 1 + B} [Ag_{++}^{(2)}(r) + g_{+-}^{(2)}(r) + Bg_{--}^{(2)}(r)] \quad (145)$$

then the fluctuations at large r will have cancelled to leave, as before, $g_m(r)$ differing from unity only at small r. If this g_m may then be identified as the pair correlation function in a non-electrolyte, only

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* Recognition of these facts forms the basis for a recent corresponding states treatment of molten salts [H. Reiss, S. W. Mayer, and J. Katz, *J. Chem. Phys.*, **35**, 820 (1961)]. Of course, the original theory of corresponding states was intended to apply only to single-component systems, but Reiss, Mayer, and Katz point out that for the special case of molten salts, only a single length parameter (the anion–cation distance of closest approach) is significant. Accordingly, the original arguments in corresponding state theory adapt easily to the two-particle salt. In spite of possible ambiguity arising from disregard of dielectric constant complications (as illustrated, for example, by explicit appearance of density derivatives in our equation of state, eq. 47), the resulting reduction of selected thermodynamic data leads to good consistency between salts.

two unknowns remain to be found. They may be denoted by φ_+ and φ_-:

$$\frac{g_{++}^{(2)}(r)}{g_{+-}^{(2)}(r)} = \exp\left[-\frac{2\varphi_+(r)}{kT}\right] \qquad (146)$$

$$\frac{g_{--}^{(2)}(r)}{g_{+-}^{(2)}(r)} = \exp\left[-\frac{2\varphi_-(r)}{kT}\right] \qquad (147)$$

A straightforward generalization of the procedure used earlier for derivation of the φ equation now leads to a simultaneous *pair* of nonlinear integral equations for φ_+ and φ_-, each involving g_m. On account of the coupling between these equations, the task of numerically constructing simultaneous self-consistent solutions, φ_+ and φ_-, is correspondingly more difficult, though probably within the range of possibility.

The trouble in this procedure is that A and B are undetermined. We only know that A and B both approach $1/2$ as the ion core forces become identical in charge-symmetric salts. In the absence of knowledge of A and B, it is provisionally possible to suppose that g_m is to be defined as the correlation function for all particle pairs regardless of species. A and B then are simple rational numbers determined by the ion valences,* or what amounts to the same thing for these electroneutral liquids, the fraction of the total number of particles which are of each type. The specific form for g_m to be used in constructing φ_+ and φ_- would be the total particle correlation function for the non-electrolyte mixture of discharged ion cores.

In conclusion, it is necessary to stress what appear to be the major tasks of the future for the theory of fused salt pair correlation functions:

(*1*) Construction of accurate solutions φ to the non-linear integral equation 138 with g_m's corresponding to several reasonable choices for the short-range interactions.

(*2*) Investigation of the accuracy of the superposition approximation (eq. 137) in electrolytes.

(*3*) Analysis of the theory of the correlation functions for general salts either to place our conjecture of the proper definition of g_m on a firmer basis, or to propose a more suitable alternative.

* For a 2-1 salt such as $CaCl_2$, for instance:

$$g_m(r) = \tfrac{1}{9}g_{++}^{(2)}(r) + \tfrac{4}{9}g_{+-}^{(2)}(r) + \tfrac{4}{9}g_{--}^{(2)}(r)$$

VII. Molten Salt Surface Tensions and the Solubility of Noble Gases

Section V.2 on the "hole" theory indicated the relevance of a liquid's surface tension to the molecular nature of bulk properties for that liquid.   In particular, this theory claims that under ordinary pressure conditions, it is almost exclusively the surface tension contribution toward their formation that determines the size distribution of "holes" in the liquid.   We now shall take up in some
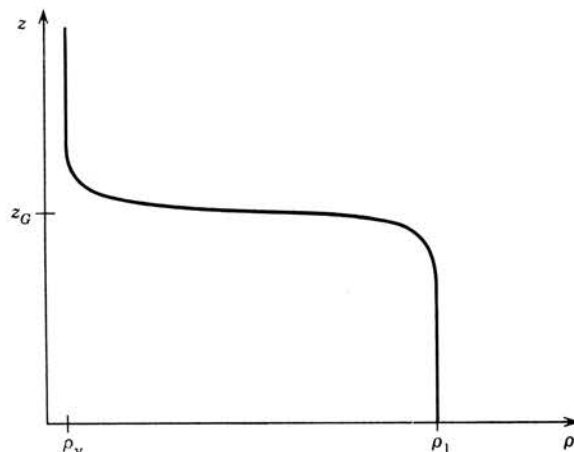

Fig. 12. Total ion density profile, $\rho(z)$, in the liquid–vapor interfacial region. z_G is the position of the equimolar dividing surface.

detail the problem of what is involved in computing molten salt surface tensions from first principles, and simultaneously arrive at information that may be used to evaluate some of the hypotheses underlying the hole theory. Specifically, the average amount of work necessary to create a spherical cavity in the fluid (which is required by the hole theory), may be found by a detailed molecular computation. This latter quantity may in turn be related to a Henry's law constant for solubility of noble gases in the melt.

We begin this discussion with a review of the basic thermodynamics of the planar liquid–vapor interface.   Figure 12 shows a typical plot of total ion density $\rho(z)$, depending on vertical coordinate z, as we pass upward in a two-phase system through the interface.   Gravity, of course, constrains the denser liquid to the lower region of the vessel.

ρ is a sum of the individual z-dependent densities, ρ_α, for each ionic species present,

$$\rho(z) = \sum_\alpha \rho_\alpha(z) \tag{148}$$

and each of these quantities is virtually independent of z except for a narrow transition region of perhaps several ionic diameters width under normal conditions of liquid–vapor coexistence. As the critical point is approached, the liquid and vapor phase bulk densities ρ_1 and ρ_v approach one another, and simultaneously the transition region is presumed to become arbitrarily wide. Just above the ordinary melting point, though, the fused salt density profile $\rho(z)$ should be very nearly discontinuous.

The equimolar Gibbs dividing surface, a plane parallel to the interface at height z_G, is defined by the condition that if $\rho(z)$ were truly discontinuous from ρ_1 to ρ_v across this plane, the total number of particles in the system implied by this density would be equal to the actual number, N. In more explicit terms, z_G is the solution of the equation:

$$\rho_1 \int_{z_B}^{z_G} dz + \rho_v \int_{z_G}^{z_T} dz = \int_{z_B}^{z_T} \rho(z)dz \tag{149}$$

where z_B and z_T are the values of z at the bottom and the top of the vessel, respectively. Since each of $\rho(z)$, ρ_1, and ρ_v are positive, the value z_G is uniquely defined by equation 149.

If the bulk thermodynamic properties of the vapor (v) and liquid (l) phases persisted rigorously up to the Gibbs dividing surface, the energy differential for the entire system would by definition be that for the two phases separately:

$$\begin{aligned} dE_v &= TdS_v - pdV_v + \mu_\pm dN_v \\ dE_1 &= TdS_1 - pdV_1 + \mu_\pm dN_1 \end{aligned} \tag{150}$$

Here, N_v and N_1 are to be interpreted as the total number of ionic particles in the vapor or liquid phase, respectively, and so $\mu_\pm$ is the mean chemical potential per particle. Thermodynamically, of course, the overall electroneutrality condition on electrolytes demands that the pure molten salt be considered as a single component. $\mu_\pm$ and T are equal in the two phases as a general result of thermodynamic equilibrium, and p is likewise the same for planar interfaces,

if one neglects gravitationally induced hydrostatic heads. As usual, the phase entropies are denoted by S_v and S_l.

The true energy differential, dE, for the actual two-phase system, where properties change continuously through the interfacial region, is not just given by the sum of dE_v and dE_l. There is additionally an excess interfacial contribution to the energy associated with the resistance of the system to increase of interfacial area $\mathfrak{a}$. If σ denotes the surface tension, the actual expression for dE must be

$$dE = T dS - p dV + \mu_{\pm} dN + \sigma d\mathfrak{a} \tag{151}$$

where

$$V = V_v + V_l, \qquad N = N_v + N_l$$

S is the actual system entropy which, on account of possible peculiar arrangements of ions in the transition region, cannot be set equal to $S_v + S_l$.

If both equations 150 are subtracted from equations 151, we obtain a relation between the specifically interfacial quantities:

$$d(E - E_v - E_l) = T d(S - S_v - S_l) + \sigma d\mathfrak{a} \tag{152}$$

The parameters T and σ are intensive variables, i.e., they do not depend on the size of the two-phase system. Accordingly, differential relation 152 may be integrated along a path of constant T and σ from zero system size to the actual container size, giving*

$$E - E_v - E_l = T(S - S_v - S_l) + \sigma \mathfrak{a} \tag{153}$$

or

$$E_a = T S_a + \sigma \tag{154}$$

where subscripts a refer to excess surface quantities per unit area:

$$E_a = \frac{1}{\mathfrak{a}} (E - E_v - E_l)$$

$$S_a = \frac{1}{\mathfrak{a}} (S - S_v - S_l) \tag{155}$$

---

* Operationally, this amounts to addition of particles to the system one by one, with concomitant volume increases to maintain constant fraction of material in each of the two phases.

If one takes the total derivative in equation 153 and compares the result with equation 152, there is obtained a result first derived by Gibbs (26):

$$S_a = -d\sigma/dT \qquad (156)$$

The temperature variation of the surface tension therefore is a direct and experimentally accessible measure for the excess ionic order induced by the presence of a liquid–vapor interface. When equation 155 is utilized in elimination of S_a from 154, we see in addition that the surface excess energy likewise may be obtained from measured surface tensions:

$$E_a = \sigma - T(d\sigma/dT)$$
$$= \frac{d(\sigma/T)}{d(1/T)} \qquad (157)$$

The general statistical mechanical theory of surface tension is well understood, and several comprehensive review articles are available on the subject (16,31,54). We sketch here the derivation of a general surface tension formula, for a fluid of particles with pairwise interactions, which involves the pair correlation functions
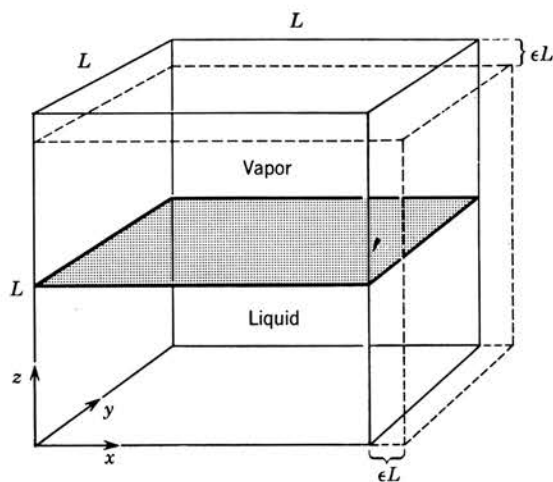

Fig. 13. Cubical vessel containing molten salt and saturated vapor, the rectangular distortion of which is considered in calculating surface tension.

in the transition region. Buff (15) was the first to apply an adaptation, to the surface case, of the procedure of Born and Green outlined in Section IV for obtaining the homogeneous system equation of state. The derivation will be presented in a form most appropriate to pure molten salts.

As shown in Figure 13, it will be assumed that the molten salt in equilibrium with saturated vapor is contained in a cubical vessel with side $L = \upsilon^{1/3}$. One proceeds to apply an infinitesimal distortion to the cube. Its vertical (z) dimension will be shrunk to $(1 - \epsilon)L$, while simultaneously the horizontal x dimension of the container will be stretched to $(1 + \epsilon)L$. To order ϵ^2, which may be assumed negligibly small, the volume is constant at $\upsilon = L^3$ during this distortion. On the other hand, the liquid–vapor interface increases in area by ϵL. If this increase is carried out isothermally, the reversible work required is just $\sigma \cdot \epsilon L$. Specifically, this work represents the difference in Helmholtz free energy, A_N, of the system in the distorted and undistorted states:

$$\sigma \epsilon L = A_N(\epsilon) - A_N(0) \tag{158}$$

Since ϵ is infinitesimal,

$$\sigma = \frac{1}{L} \left(\frac{\partial A_N}{\partial \epsilon} \right)_{\epsilon=0} \tag{159}$$

The ϵ derivative of A_N may, in principle, be computed from the canonical partition function. Analogous to the procedure in Section IV, dimensionless configuration vectors $\mathbf{s}_i$ are introduced for each ion, with components (s_{ix}, s_{iy}, s_{iz}) running between limits 0 and 1 for positions inside the distorted (arbitrary ϵ) container. Thus, to order ϵ^2,

$$\exp\left[-\frac{A_N(\epsilon)}{kT} \right] = \frac{L^{3N}}{\prod\limits_{\alpha=1}^{\mu} N_\alpha! \, \lambda_\alpha^{3N_\alpha}} \int_0^1 ds_{1x} \ldots \int_0^1 ds_{Nz}$$

$$\times \exp\left[-\frac{1}{kT} \sum_{i<j=1}^{N} V_{\gamma\delta}(r_{ij}) \right] \tag{160}$$

(particle i's species is denoted by γ, j's by δ). The Born cavity free energies which were shown in Section III to be a part of the total interaction energy have here been suppressed on the basis that the

constant volume distortion process does not change the dielectric constant of either phase.

Each pair distance r_{ij} must be regarded as a function of the reduced vectors $\mathbf{s}_i$ and $\mathbf{s}_j$, as well as of ϵ. Since it is necessary only to work to linear order in ϵ, we take

$$
\begin{aligned}
r_{ij} &= [(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2]^{1/2} \\
&= L\left\{[(1 + \epsilon)(s_{jx} - s_{ix})]^2 + (s_{jy} - s_{iy})^2 + [(1 - \epsilon)(s_{jz} - s_{iz})]^2\right\}^{1/2} \\
&\cong L\left\{s_{ij} + \frac{(s_{jx} - s_{ix})^2 - (s_{jz} - s_{iz})^2}{s_{ij}}\,\epsilon\right\} \\
s_{ij}^2 &= (s_{jx} - s_{ix})^2 + (s_{jy} - s_{iy})^2 + (s_{jz} - s_{iz})^2
\end{aligned}
\tag{161}
$$

If this form for the r_{ij}'s is inserted into the partition function (eq. 160), the derivative indicated in equation 159 may be computed in a formal sense immediately.

To cast the resulting surface tension expression into a convenient form, use may be made of definitions of the z-dependent densities $\rho_\alpha(z)$, as well as of the pair correlation function in the interfacial region, in terms of the total canonical ensemble phase space density, P_N (eq. 24). In formulating these definitions, one may transcribe the considerations of Section IV for the homogeneous system pair correlation functions to the same function in the heterogeneous case; for $\rho_\alpha(z)$, however, one inquires about the occupation probability by an α-species particle of a *single* infinitesimal volume element at height z, and in the present case of the two-phase $g_{\alpha\beta}^{(2)}$, the requisite *pair* of volume elements may be located near the transition region. One readily finds

$$
\rho_\alpha(z_1) = N_\alpha \int P_N(\mathbf{r}_1 \ldots \mathbf{p}_N) d^3\mathbf{r}_2 \ldots d^3\mathbf{p}_N
\tag{162}
$$

where integration is over all momenta, and over all positions save that of a particle of type α, here numbered 1. The normalization is such that $\rho_\alpha(z)$ properly reduces to the respective homogeneous phase density when z is well within either the liquid or the vapor. The pair correlation function result is

$$
g_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N_\alpha N_\beta}{\rho_\alpha(z_1)\,\rho_\beta(z_2)} \int P_N(\mathbf{r}_1 \ldots \mathbf{p}_N) d^3\mathbf{r}_3 \ldots d^3\mathbf{p}_N
\tag{163}
$$

(the particle numbered 2 is type β). The effect of dividing by $\rho_\alpha(z_1)\rho_\beta(z_2)$ in this expression is to retain the property of $g_{\alpha\beta}^{(2)}$ of becoming unity when $|\mathbf{r}_2 - \mathbf{r}_1|$ is large compared to the range of intermolecular forces, even when one or both of $\mathbf{r}_1, \mathbf{r}_2$ is in the interface. It is important to realize that the correlation of pairs in the interface is no longer spherically symmetric, as it is well within the bulk of either fluid phase. In the homogeneous case, equation 162 reduces to $N_\alpha/\mathcal{V}$ and equation 163 to the spherically symmetric pair correlation function previously discussed.

In view of definitions 162 and 163, it is only a matter of standard manipulation of equations 159 and 160 to show that the surface tension is given by

$$\sigma = \frac{1}{2} \sum_{\alpha,\beta} \int_{-\infty}^{+\infty} dz_1 \int d^3\mathbf{r}_{12} \frac{x_{12}^2 - z_{12}^2}{r_{12}} \frac{dV_{\alpha\beta}(r_{12})}{dr_{12}}$$

$$\times \rho_\alpha(z_1)\rho_\beta(z_2)g_{\alpha\beta}^{(2)}(z_1,\mathbf{r}_{12}) \quad (164)$$

$$\mathbf{r}_{12} = (x_{12},\, y_{12},\, z_{12})$$

For convenience, the interfacial pair correlation function has been written as a function of the height z_1 only of one particle, as well as the *relative* position $\mathbf{r}_{12}$ of the other particle. In deriving this result for σ, we have passed to the limit of infinite system size, intensive variables being held constant. On account of the qualitative features of ρ_α, ρ_β, and $g_{\alpha\beta}^{(2)}$, the $d^3\mathbf{r}_{12}$ integral in (164) is essentially vanishing unless z_1 is in the transition region. As expected, therefore, the surface tension arises entirely in this transition region, and may be associated with the anisotropy of distribution of pairs there.

For molten salts at or just above their ordinary melting points, the saturated vapor is very dilute. The surface of the liquid may be viewed approximately as a sharp discontinuity from constant liquid density ($\rho_\alpha = c_\alpha$, independent of z, is the bulk liquid number density for species α) for values of z below the equimolar dividing surface, $z = z_G$, to zero density above. Furthermore, if $g_{\alpha\beta}^{(2)}$ retains its spherically symmetric bulk liquid form for all pairs of positions below z_G, then general equation 164 reduces to a particularly simple form:

$$\sigma = \frac{\pi}{8} \sum_{\alpha,\beta} c_\alpha c_\beta \int_0^\infty dr\, r^4 \frac{dV_{\alpha\beta}(r)}{dr}\, g_{\alpha\beta}^{(2)}(r) \quad (165)$$

This result, for single-component systems, was first derived by Fowler (23). In this approximation, a knowledge of the pair correlation functions for the bulk liquid then suffices to allow estimation of the molten salt surface tension. Equation 165 is expected to break down as the critical point is approached on account of non-negligible vapor density, as well as widening of the transition region.

The attraction of Fowler's expression for σ is that it avoids the very difficult problem of computing details of each $\rho_\alpha(z)$, and the non-spherically symmetric interfacial pair correlation functions. Furthermore, we may deduce from it an interesting relation for the surface tension of a special class of salts. For those salts which are of the symmetrical valence type, and whose ions have identical short-range pair interaction $V^{(s)}(r)$, the ion pair potentials may be written:

$$V_{\alpha\beta}(r) = V^{(s)}(r) + \frac{(ze)^2}{Dr}\,\xi_\alpha\xi_\beta$$

$$\xi_+ = -\,\xi_- = 1 \tag{166}$$

Inserting this into Fowler's expression (eq. 165), with $c_+ = c_- = c$ for this symmetrical electrolyte,

$$\sigma = \frac{\pi c^2}{2}\int_0^\infty dr\,r^4\,\frac{dV^{(s)}(r)}{dr}\,g_m(r) - \frac{\pi(cze)^2}{4D}$$

$$\times \int_0^\infty dr\,r^2[g_{++}^{(2)}(r) - g_{+-}^{(2)}(r)] \tag{167}$$

Use has been made here of the definition of the mean correlation function g_m (eq. 123) and the identity of $g_{++}^{(2)}$ and $g_{--}^{(2)}$ for this simple class of salts.

The second integral in the last equation is exactly that occurring in the local electroneutrality condition (eq. 143) and on this basis may be eliminated. The first integral, involving $V^{(s)}$, also may be simplified if this short-range potential is assumed equal to that for pairs of rigid spheres with diameter a:

$$V^{(s)}(r) = +\infty \qquad r < a$$

$$= 0 \qquad r \geq a \tag{168}$$

Although this specific choice for $V^{(s)}$ formally makes the first integral in equation 167 undefined, a careful analysis (42) shows that if the rigid sphere interaction is treated as the limit of a well-behaved (i.e., bounded and differentiable) function, the integral properly approaches a finite limit:

$$\int_0^\infty dr\, r^4\, \frac{dV^{(s)}(r)}{dr}\, g_m(r) \to -\, kTa^4 g_m(a) \qquad (169)$$

Only that value of g_m occurs corresponding to contact between the rigid cores. Upon utilizing these two identifications, the surface tension becomes

$$\sigma = -\, \frac{\pi kT c^2 a^4}{2}\, g_m(a) + \frac{c(ze)^2}{16D} \qquad (170)$$

According to the ideas of Section VI, $g_m(a)$ should virtually be equal to the pair correlation function for the set of uncharged hard sphere (HS) ion cores in the same volume $\mathcal{V}$ as the molten salt:

$$g_m(a) \cong g_{\mathrm{HS}}^{(2)}(a) \qquad (171)$$

The interesting feature of result 170 is the extremely simple way in which the effect of Coulomb interactions appears; specifically, it is just the second term, $c(ze)^2/16D$. The leading, non-electrostatic contribution should be nothing more than the surface tension remaining, σ_{HS}, when all the ions have been discharged. One must realize in this case it is conceptually necessary to maintain the sharp interface between a negligible density vapor and the liquid by means of a rigid retaining wall, for in the absence of Coulomb forces, no liquid–vapor coexistence is possible.

In connection with evaluation of σ_{HS}, it should be noted that $g_{\mathrm{HS}}^{(2)}(a)$ is a well-known and extensively investigated quantity. By its definition, it must obviously be positive, so σ_{HS} is predicted to be always negative. From the theory of the rigid sphere equation of state (35), $g_{\mathrm{HS}}^{(2)}(a)$ may be rigorously and simply exhibited in terms of the pressure for that fluid:

$$g_{\mathrm{HS}}^{(2)}(a) = \frac{3}{2\pi\rho a^3}\left[\left(\frac{p}{\rho kT}\right)_{\mathrm{HS}} - 1\right] \qquad (172)$$

ρ denotes the total liquid-phase density of rigid spheres, $2c$. This contact correlation presumably may be estimated by high-tem-

perature equation of state measurements on noble gases at the proper density. Alternatively, we may use the very accurate results for this quantity computed by Reiss et al. (60):

$$g_{HS}^{(2)}(a) = \frac{4 - 2y + y^2}{4(1 - y)^3}$$

$$y = \frac{\pi}{6}\,\rho a^3 = \frac{\pi}{3}\,ca^3 \tag{173}$$

In view of identification 171, the simple surface tension expression (eq. 170) exhibits temperature dependence from four sources. First, there is the explicit appearance of T in this expression. Secondly, thermal expansion of the liquid causes a small variation in c. Additionally, this change in c brings about changes in $g_{HS}^{(2)}(a)$, and in the dielectric constant, D. Since the thermal expansion of molten salts is not large, one may suppose that the temperature change of σ arises predominantly from the first source, and so a means is readily available for estimating coefficients in the linear temperature law (6) observed for molten salt surface tensions.

Consistent with the Fowler picture of a discontinuous density at the interface would be a simple direct computation of the surface energy, E_a. Neglecting the salt's thermal expansion, with consequent temperature variation of $g_{HS}^{(2)}(a)$ and D, insertion of equation 170 into equation 157 yields

$$E_a = \frac{c(ze)^2}{16D} \tag{174}$$

The rigid core thus gives no contribution to the excess surface energy. This simple expression indicates that E_a should exhibit temperature variation only to the very small extent induced by liquid thermal expansion. If general relation 157 is utilized in computing E_a from experimentally measured surface tensions, the results should be considerably more constant over a wide temperature range than the surface tensions themselves. Such behavior has in fact been noticed by Bloom et al. (7), and the present analysis constitutes at least a partial theoretical explanation.

Reiss, Frisch, Helfand, and Lebowitz (RFHL) (59) have developed a statistical mechanical theory for the amount of reversible work, $W(r)$, necessary to introduce a spherical cavity of radius r into a

liquid, the interior of which is rigorously free of molecules. Not only is it possible to deduce a surface tension from their results (for the cavity–liquid interface), but in addition, the small-cavity work may be compared with the same quantity occurring in the "hole theory." Although this latter approach, as indicated in Section V.2, usually claims to permit the possibility of evaporation into the cavities, or holes, ordinary molten salts have such low vapor pressures that these events may be presumed unlikely. As a consequence, the RFHL cavity formation work should be very closely identifiable with the hole formation work.

Finally, this reversible cavity creation work may be used to calculate the solubility of simple gases in the fused salt, since a major contribution to the free energy of solution is the free energy associated with displacement of liquid particles to form a region of sufficient size to contain the dissolved atom or molecule (59). The RFHL analysis up to the present has been developed only for liquids whose particles conform to an equal sized rigid molecular core model; the "soft" portion of the pair potentials need not generally be specified, though for the molten salt case they must obviously be at least partially Coulombic.
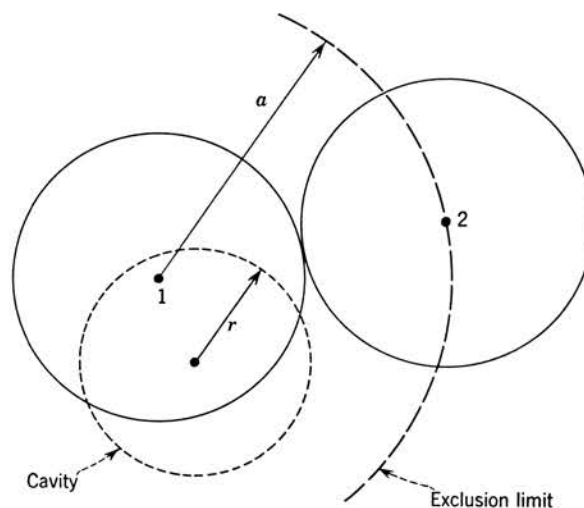

Fig. 14. Diagram illustrating the rigorous exclusion of other molecular centers, such as *2*, when one molecular core *1*, of diameter a is centered within the cavity of radius $r \leq a/2$.

We shall briefly review the RFHL method. If the rigid core diameter of liquid particles is once again denoted by a, the value of $W(r)$ for $0 \leq r \leq a/2$ may be written down exactly. This fact results from observation that for these small values of r, at most one molecular center could have been contained within the spherical cavity region, were it not for the condition that this region be empty. When one particle has its center there, its repulsive core force range completely overlaps the cavity, and so rigorously excludes other particles from this region (see Fig. 14). For all values of r, $W(r)$ is related to q_0, the probability that a spontaneous local density fluctuation has emptied the fixed cavity region, by a Boltzmann expression:

$$\exp\left[-\frac{W(r)}{kT}\right] = q_0 \tag{175}$$

But for the special case $0 \leq r \leq a/2$, q_0 is unity minus the single particle occupation probability, q_1:

$$q_0 = 1 - q_1$$
$$= 1 - \frac{4\pi r^3}{3}\rho \tag{176}$$

Consequently,

$$W(r) = -kT \ln\left(1 - \frac{4\pi r^3}{3}\rho\right) \qquad 0 \leq r \leq a/2 \tag{177}$$

For large values of r, we know from macroscopic considerations that the asymptotic form of $W(r)$ is just the sum of volume expansion and surface tension works:

$$W(r) \sim 4\pi\sigma r^2 + {}^4/_3\pi p r^3 \qquad \text{(large } r\text{)} \tag{178}$$

as already used in the hole theory, equation 64. It may generally be demonstrated, though, that σ should begin to show a curvature dependence for spherical interfaces (the cavity surface) whose radii of curvature are comparable with the range of molecular sizes. The consequence so far as $W(r)$ is concerned is that expression 178 becomes inadequate for r comparable with a, if σ is taken to be an r-independent constant. The scheme devised by RFHL is to take the curvature dependence of σ explicitly into account by writing $W(r)$ in the form:

$$W(r) = K_0 + K_1 r + 4\pi\sigma_\infty r^2 + {}^4/_3\pi p r^3 \qquad (179)$$

for all $r \geq a/2$, where σ_∞ is the asymptotic value of σ for infinite radii of curvature (planar interface).

It may be shown on a very general basis (59) that $W(r)$, as well as its first and second r derivatives, must be continuous at $r = a/2$. These conditions are sufficient to determine K_0 and K_1, when the exact form (eq. 177) for $W(r)$ is used for $r \leq a/2$. Simultaneously, the planar cavity–liquid interfacial tension σ_∞ is obtained in terms of the total particle density ρ (or equivalently, $y = {}^1/_6\pi\rho a^3$) and the pressure p. One finds:

$$K_0 = kT\left\{-\ln(1-y) + \frac{9}{2}\left(\frac{y}{1-y}\right)^2\right\} - \frac{\pi p a^3}{6}$$

$$K_1 = -\frac{kT}{a}\left\{\frac{6y}{1-y} + 18\left(\frac{y}{1-y}\right)^2\right\} + \pi p a^2 \qquad (180)$$

$$\sigma_\infty = \frac{3kT}{2\pi a^2}\frac{y(2-y)}{(1-y)^2} - \frac{pa}{2}$$

The implication behind this calculation, as in application of the Fowler method, is that the sharp density discontinuity at the cavity

TABLE II

Comparison of Alkali Halide Surface Tensions Computed by Means of Equation 180 with Experimental Values. [From H. Reiss and S. W. Mayer, *J. Chem. Phys.*, **34**, 2001 (1961).] Units are dynes/cm.

	T, °C.	σ (obs.)	σ (calc.)
NaCl	1000	98	111
NaBr	900	91	95
NaI	700	84	75
KCl	900	90	96
KBr	800	85	87
KI	800	69	76
RbCl	828	89	81
RbBr	831	81	83
RbI	772	72	72
CsF	826	96	85
CsCl	830	78	79
CsBr	808	72	76
CsI	821	63	70

boundary, for cavities sufficiently large to approach locally a planar surface, may adequately represent the liquid–vapor interface. One may therefore compare surface tensions σ_∞ computed from the last of equations 180 with the measured values for molten salts with equal sized cores. If, furthermore, the ideas of the preceding section are correct, concerning application of the equal-sized ion model to the wider class of salts with moderately differing anion and cation sizes, then the σ_∞ formula should still be useful if a is interpreted as the anion–cation distance of nearest approach. Table II presents a comparison of experimental data with numerical results obtained on this basis by Reiss and Mayer.

It is interesting to note that surface tensions that have been computed for single-component non-electrolytes (59) from equation 180 are invariably high, though reasonably accurate. This trend is not difficult to understand and is connected with use of an unphysical density discontinuity to represent the interface. If one imagines first an impenetrable planar membrane enforcing this rigorous discontinuity, then removal of this constraint would immediately be followed by a spontaneous motion of interfacial material, in the form of widening of the transition region. This spontaneous relaxation process must be equivalent to a decrease in free energy, so that the true surface tension (since it is a surface free energy per unit area) must be less than that for a sharp interface. When, finally, equation 180 is applied to fused salts, each computed σ_∞ should be regarded as an upper bound for the corresponding experimental quantity.

Aside from the discontinuity simplification inherent in both the Fowler and the RFHL procedures, we notice that only the former finds it necessary to assume a very special form for the correlation of particle pairs in the interfacial region. This fairly drastic assumption probably implies that Fowler's formula (eq. 165) for surface tension is generally less reliable than σ_∞ in equation 180. In this connection, it is informative to compare σ_{HS}, the leading term of equation 170 where $g_m = g_{HS}$, with the value of σ_∞ predicted for uncharged hard spheres using equations 172 and 173 for the hard sphere pressure:

$$\sigma_{HS} = -\frac{9kTy^2}{8\pi a^2} \cdot \frac{4 - 2y + y^2}{(1 - y)^3} \quad \text{(Fowler)}$$

$$(\sigma_\infty)_{HS} = -\frac{9kTy^2}{8\pi a^2} \cdot \frac{4 + 4y}{(1 - y)^3} \quad \text{(RFHL)}$$

$$(181)$$

Both results agree to lowest order in y and are always negative when y is in the range of physically accessible values $0 \leq y \leq 0.740$ (close-packed spheres). By way of indicating the order of magnitude error inherent in the interface pair correlation approximation of Fowler's method, Table III compares these two surface tensions for

TABLE III

Comparison of the Rigid Sphere Surface Tensions Computed on the Basis of Fowler's Formula (middle column), and the RFHL Theory (last column)

y	$-\dfrac{8\pi a^2}{9kT}\sigma_{\text{HS}}$	$-\dfrac{8\pi a^2}{9kT}(\sigma_\infty)_{\text{HS}}$
0.1	0.052	0.060
0.2	0.248	0.375
0.3	0.916	1.365
0.4	2.489	4.148
0.5	6.500	12.000
0.6	17.770	36.000
0.7	56.078	123.407

various y. For dense fluids, there is a discrepancy amounting to about a factor of 2. This fact suggests that improvement of equation 170 would result (at least for discontinuous density interfaces) if $(\sigma_\infty)_{\text{HS}}$ is used in place of the leading term in this expression.

In discussing the hole theory in Section V.2, it was pointed out that the mean hole size in molten salts should be roughly comparable to the ions forming the liquid. If this is the case, then the curvature dependence of the surface tension should be rather important in the formation work for most holes, though traditionally this curvature dependence is disregarded. If, for example, one computes the work $W(r = a)$ necessary to open up a cavity in the uncharged rigid sphere fluid just big enough to contain one more sphere, first without (W_1) and then with (W_2) curvature corrections,

$$W_1 = 4.34kT$$
$$W_2 = 7.77kT \tag{182}$$

These numbers refer to the half close-packed density for the spheres, $y = 0.370$, corresponding to dense liquids. As a result, one must conclude that the curvature corrections are not negligible (the error in this example is 44%). It therefore seems worthwhile to have the

hole theory reformulated with these corrections. Of course, the results (eqs. 182) refer only to the special rigid sphere non-electrolyte, but it is hard to believe that similar discrepancies are not to be found for fused salts, or for that matter, in any real liquid.

Besides providing a certain amount of information about possible hole theory refinements, the cavity creation work $W(r)$ is useful in another connection. It is possible to obtain an estimate of the Henry's law constant, k_H, for solution of gases in the melt (59). k_H is defined as the ratio of dissolving gas partial pressure, p_g, in the dilute gas phase, to the concentration dissolved in the melt, ρ_g:

$$k_H = p_g/\rho_g \tag{183}$$

The condition which determines at equilibrium simultaneous values of p_g and ρ_g is that the chemical potential for the dissolving substance be the same in vapor and liquid phases. We may suppose that this substance is an ideal gas in the vapor phase so, its chemical potential there is

$$\mu_g^{(v)} = kT \ln [p_g \lambda_g^3/kT] \tag{184}$$

λ_g is the mean thermal deBroglie wavelength for the dissolving gas.

In the liquid, the solute chemical potential may be taken as the form appropriate to dilute solutions:

$$\mu_g^{(l)} = kT \ln \rho_g \lambda_g^3 + W_c^{(g)} \tag{185}$$

The quantity $W_c^{(g)}$ represents the isothermal reversible work required to transfer one of the gas particles to the interior of the liquid phase.

Three contributions to $W_c^{(g)}$ may be distinguished,

$$W_c^{(g)} = Y_1 + Y_2 + Y_3 \tag{186}$$

In order that the solute particle be able to fit into the liquid medium, it is necessary that the constituent particles of the solvent be moved aside to make room for it. This work, Y_1, is thus a cavity creation work; if the solute particle has short-range repulsive forces which act sufficiently like a sphere of diameter a_g, while those of the salt ions are still characterized by rigid sphere diameter a, then we may take

$$Y_1 = W\left(\frac{a_g + a}{2}\right) \tag{187}$$

using equation 179 for W.

In addition, the solute particle will have short-range forces outside the closest approach distance to the ions. These latter interactions, which we might denote by $V_{g\alpha}{}^{(s)}(r)$ for the pair potential between the gas particle and an α-species ion, will be predominantly attractive, and we shall suppose by definition this interaction does not include polarization forces. For many gases, $V_{g\alpha}{}^{(s)}(r)$ will be rather small in magnitude compared with kT at molten salt temperatures. Therefore the average arrangement of ions around the solute particle will be virtually unchanged by the presence of $V_{g\alpha}{}^{(s)}(r)$ outside the hard core; as a consequence, the extra free energy of placing the solute particle in the fused salt arising from $V_{g\alpha}{}^{(s)}$ is just the *energy* of interaction:

$$Y_2 = 4\pi \sum_{\alpha=1}^{\mu} c_\alpha \int_{(a_g+a)/2}^{\infty} V_{g\alpha}{}^{(s)}(r) g_{g\alpha}{}^{(2)}(r) r^2 dr \tag{188}$$

The $g_{g\alpha}{}^{(2)}(r)$ are the pair correlation functions acting in the fused salt between the dissolved gas atom and α-species ions.

The final contribution to $W_c{}^{(g)}$, Y_3, is associated with the fluctuating electric field present at the position of the dissolved particle, and due to thermal motions of the neighboring ions. If we suppose that the only effect of this fluctuating field $\mathbf{E}$ is to induce instantaneously a dipole $\alpha_g \mathbf{E}$ in the dissolved molecule (its polarizability is α_g), then the mean polarization energy of this gas molecule is

$$Y_3 = -\tfrac{1}{2}\alpha_g \langle E^2 \rangle \tag{189}$$

which requires knowledge only of the mean square field $\langle E^2 \rangle$ at its center, rather than other details of $\mathbf{E}$.

To complete the picture, it is necessary to point out that $\langle E^2 \rangle$ has a straightforward representation in terms of the distribution of ions around the central solute particle. Since the instantaneous value of $\mathbf{E}$ is

$$\mathbf{E} = -\nabla_{\mathbf{r}_g} \sum_{i=1}^{N} \frac{(ze)\xi_i}{Dr_{gi}}$$
$$r_{gi} = |\mathbf{r}_i - \mathbf{r}_g| \tag{190}$$

when the solute particle is located at $\mathbf{r}_g$, and the N ions at $\mathbf{r}_1 \ldots \mathbf{r}_N$, a canonical ensemble average of E^2 by the techniques of Section IV lead at once to the expression required:

$$\langle E^2 \rangle = \left(\frac{ze}{D}\right)^2 \left\{ \sum_{\alpha=1}^{\mu} c_\alpha \xi_\alpha^2 \int \frac{1}{r_{g\alpha}^4} g_{g\alpha}{}^{\prime(2)}(r_{g\alpha}) d^3\mathbf{r}_\alpha \right.$$

$$\left. + \sum_{\alpha,\beta=1}^{\mu} c_\alpha c_\beta \xi_\alpha \xi_\beta \int \frac{\mathbf{u}_{g\alpha}\cdot\mathbf{u}_{g\beta}}{r_{g\alpha}^2 r_{g\beta}^2} g_{g\alpha\beta}{}^{(3)}(\mathbf{r}_g,\mathbf{r}_\alpha,\mathbf{r}_\beta) d^3\mathbf{r}_\alpha d^3\mathbf{r}_\beta \right\} \quad (191)$$

$$\mathbf{u}_{g\alpha} = \frac{\mathbf{r}_{g\alpha}}{|\mathbf{r}_{g\alpha}|} \qquad \mathbf{u}_{g\beta} = \frac{\mathbf{r}_{g\beta}}{|\mathbf{r}_{g\beta}|}$$

Rigorous evaluation of $\langle E^2 \rangle$ therefore demands not only the solute–ion pair correlation functions, but the solute–ion–ion triplet functions $g_{g\alpha\beta}{}^{(3)}$ as well. Although apparently no serious use of equation 191 has yet been made in computing gas solubilities, it will presumably be necessary in doing so to use a superposition approximation to reduce such $g^{(3)}$ to a product of $g^{(2)}$'s. In this event, a further demonstration of the utility and informative nature of molten salt pair correlation functions is provided.

The final form of the Henry's law constant, obtained by equating liquid and vapor phase chemical potentials, is

$$k_H = kT \exp\left[\frac{1}{kT}(Y_1 + Y_2 + Y_3)\right] \quad (192)$$

No direct experimental confirmation of this detailed solubility theory is yet available for pure salts. However, Blander et al. (2) have measured noble gas solubilities in mixed fluoride melts. The relevant k_H have been computed neglecting Y_2 and Y_3, and estimating Y_1 as just the product of the macroscopic liquid–vapor planar interfacial tension, times the surface area of the solute-containing cavity. Agreement is obtained only in correct order of magnitude.

In conclusion, we must acknowledge that in these surface tension considerations it has implicitly been assumed that the ions were subject to the same type of potential energy as was adopted for the bulk liquid, i.e., a sum of pairwise additive interactions supplemented by the position-independent Born cavity energies. It will be recalled, though, that the dielectric properties as examined in Section III supposed that the molten salt medium was both homogeneous and isotropic. This is obviously appropriate for the interior of a single liquid phase, but if the computation is repeated in the presence of a liquid–vapor interface, two modifications are in the strict sense required for the potential energy of the system. In the first place,

each Born cavity energy, $U_{bc}{}^{(\alpha)}$, changes continuously as the interface is traversed from its position-independent negative value in the interior of the liquid, to generally a much different value in the dilute vapor. For fairly large distances from the interface on the liquid side, this modification yields the so-called "image potential" of a charge near a planar dielectric discontinuity, familiar from elementary electrostatics (64). On this basis, ions at the interface would experience a less negative Born cavity energy (that is, they are repelled from the interface), and since an increase in surface area increases the number of such ions, one concludes that this modification is in the direction of increasing surface tension.

The second modification required is that each ion pair interaction $V_{\alpha\beta}(r)$ is itself subject to variation in the interfacial region (from its bulk liquid form) because it, too, depends upon dielectric properties there. Once again this change, for r not too small, and if the ions are not too near the interface, may be interpreted in terms of images.* Qualitatively, the result amounts to interaction of one ion in the chosen pair with the image of the other, and vice versa. Because this implies enhanced negative interaction for unlike ion pairs (the most common nearest neighbor type), the tendency is for these pairs to be attracted to the interface, so this second modification should have the opposite effect on the surface tension as the first.

A scrupulously detailed theory of the molten salt interfacial properties naturally would have to take account of these elaborations. But in view of the present quantitatively uncertain position of the theory in dealing with these surfaces, it seems worthwhile to present the simpler results for evaluation first, before refinements are added.

* The relevant computations for both modifications have been carried out in connection with surface properties of electrolytic solutions (17).

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