

The extension of macroscopic classical hydrodynamics to the microscopic regime is a difficult procedure to evaluate. Since, as shown by the numerical example, holes in fused salts are comparable in size to the ions forming these liquids, it seems very likely that appreciable corrections to the continuum hydrodynamic calculation of m_r and m_t are necessary.

Finally, the use of a macroscopic surface tension to describe very small spherical interfaces is risky business, though probably correct in qualitative features. The curvature corrections to σ that are possible with presently available theory will be discussed in Section VII, where surface tensions will be scrutinized at some length. Indications are that such refinements are important.

C. A LATTICE THEORY

As a final example of an approximate theory of fused salts, we shall outline a liquid-state lattice theory for these substances. Unlike the significant structures theory and the hole theory, we start from the explicit form of the canonical partition function, and stepwise proceed in derivation of a lattice theory of simple molten electrolytes, making clear at each stage what approximations are necessary. As developed here, this molten electrolyte lattice theory is designed ultimately to evaluate not only the configurational contribution to thermodynamic properties, from fundamentals, but also certain gross features of ionic arrangement in the melt. Ideally, this approach would have no adjustable parameters, and so should be open to direct evaluation as a model for molten salts, without the specious and often misleading fit to experimental data that could lead to acceptance of incorrectly derived semiempirical theories.

A motivation for study of a molten salt lattice theory arises from the considerable interest in, and success with, liquid-state cell (or lattice) theories for non-electrolytes (58). It is therefore important, in a survey of molten salts, to understand what requirements are placed upon an application of these methods to assemblies of electrostatically charged particles. In particular, the use of just nearest neighbor interactions, as usually is sufficient in ordinary lattice or cell theories, now becomes manifestly impossible. We therefore propose here a technique for including the long-range Coulomb forces in a lattice theory.

The basic idea of the lattice theory of liquids is subdivision of the

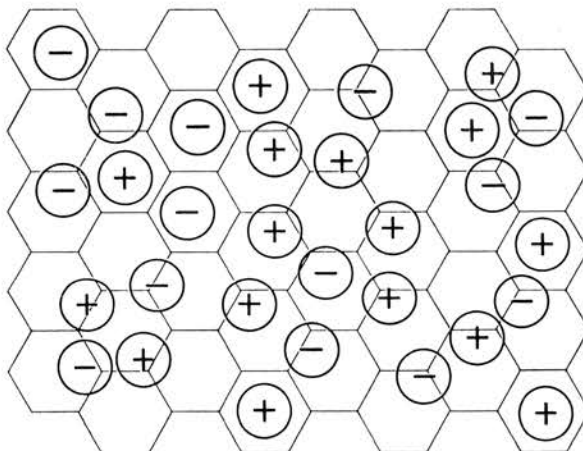


Fig. 8. Subdivision scheme of the fused salt volume into identical cells with molecular dimensions. Ions are regarded as occupying cells in which their centers lie. Some cells are empty on account of liquid-state configurational randomness, and resultant microscopic density fluctuations.

actual physical space occupied by the liquid into a set of small volume elements, or cells. This subdivision is represented for an hypothetical two-dimensional fluid in Figure 8. These cells will be chosen to form a regular lattice, so they will all be identical in size and shape. The cells will be comparable in size to molecular dimensions.

The rigorous canonical partition function for the molten salt, Q_N , has already been written in equation 29. For the present purposes, the Born cavity energy may be subtracted from the total potential V_N , to leave a partition function, Q_{cell} , of the form:

$$\begin{aligned}
 Q_{\text{cell}} &= \exp \left[- \frac{1}{kT} \left(A_N - \sum_{\alpha=1}^{\mu} N_{\alpha} U_{bc}^{(\alpha)} \right) \right] \\
 &= \frac{1}{\prod_{\alpha=1}^{\mu} N_{\alpha}! \lambda_{\alpha}^{3N_{\alpha}}} \int_{\mathbf{v}} d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \exp \left\{ - \frac{1}{kT} \sum_{i<j=1}^N V_{\gamma\delta}(r_{ij}) \right\}
 \end{aligned} \tag{78}$$

The integrand now contains only the total particle pair potentials, $V_{\gamma\delta}(r_{ij})$, for a pair of ions i, j of species γ and δ , respectively:

$$V_{\gamma\delta}(r_{ij}) = V_{\gamma\delta^{(s)}}(r_{ij}) + V_{\gamma\delta^{(e)}}(r_{ij})$$

(see eq. 24). Since the limits of integration for the variable configuration vectors $\mathbf{r}_1 \dots \mathbf{r}_N$ include all sets of positions inside the container volume \mathcal{V} , each of the N ions may conceivably occupy at any time any one of the cells which \mathcal{V} comprises.

Each of the cells will be identified by an index j , $1 \leq j \leq \Omega$, where the number of cells Ω is \mathcal{V} divided by the cell volume, ω . Q_{cell} may then formally be written as a sum over all ways of placing the N ions in the various cells, of integrals over positions of the ions within those cells only:

$$Q_{\text{cell}} = \frac{1}{\prod_{\alpha=1}^{\mu} N_{\alpha}! \lambda_{\alpha}^{3N_{\alpha}}} \sum_{j_1 \dots j_N=1}^{\Omega} \int_{\omega_{j_1}} d^3\mathbf{r}_1 \int_{\omega_{j_2}} d^3\mathbf{r}_2 \dots \int_{\omega_{j_N}} d^3\mathbf{r}_N \exp \left\{ -\frac{1}{kT} \sum_{i<j=1}^N V_{\gamma\delta}(r_{ij}) \right\} \quad (79)$$

Many of the ways of placing ions in the cells result in precisely the same value for the integral in equation 79. In particular, it matters only what species ion is contained in a given cell, but not which specific one of these ions resides there. As a consequence, we may lump together all such terms in equation 79, of which there are exactly as many as the number of ways of distributing the ions among cells, maintaining a constant number of each sort in each cell.

At this early stage, it proves to be a handy simplification to choose the cell size small enough that occupancy by more than just a single ion is a sufficiently rare event to neglect. Since double or multiple occupancy must be prevented by the short-range repulsive ion core forces, the acceptable range of cell sizes will vary according to the salt of interest. The number of equivalent distributions of ions so far as equation 79 is concerned, is now precisely

$$\prod_{\alpha=1}^{\mu} N_{\alpha}!$$

which cancels an identical factor in the denominator of that equation.

For a single pure fused salt having only single anionic and cationic species, we may assign an "occupation parameter," ξ_j , to each cell, ω_j . This parameter will be $+1$ if a cation is in cell ω_j , 0 if the cell is empty, and -1 if an anion resides there. The admissible sets of occupation

parameters, $\{\xi_j\}$, must be consistent with the fixed numbers of anions, cations, and vacant cells in the system.

The advantage of use of the ξ 's is that an effective lattice-theory interaction, $\tilde{V}_\Omega(\xi_1 \dots \xi_\Omega)$, may be defined which allows the integral representation of Q_{cell} (eq. 79) to be replaced entirely by a sum over acceptable sets, $\{\xi_j\}$:

$$Q_{\text{cell}} = \prod_{\alpha=1}^{\mu} \left(\frac{\omega}{\lambda_{\alpha}^3} \right)^{N_{\alpha}} \sum'_{\{\xi_j\}} \exp \left\{ - \frac{1}{kT} \tilde{V}_\Omega(\xi_1 \dots \xi_\Omega) \right\} \quad (80)$$

The primed summation indicates admittance of only proper sets $\{\xi_j\}$. If the cells were sufficiently small that position variations of ion centers within these cells results in negligible variation in the ion pair potentials, $\tilde{V}_\Omega(\xi_1 \dots \xi_\Omega)$ could confidently be set equal to

$$\sum_{i < j = 1}^N V_{\gamma\delta}(r_{ij})$$

where the various r_{ij} might be taken, say, as the distance between centers of cells supposed to be occupied by the corresponding ion types, as dictated by $\{\xi_j\}$. Since each integral in equation 79 would therefore have an integrand virtually constant over the region of integration, and equal to

$$\exp \left\{ - \frac{1}{kT} \tilde{V}_\Omega \right\}$$

equation 80 follows immediately.

However, if ω is large enough to allow appreciable interaction variations, a more elaborate definition of \tilde{V}_Ω is necessary. We may first inquire, under this circumstance, what would be the proper form of \tilde{V}_Ω if all cells were vacant with the exception of ω_i and ω_j . In this case, reduction of the integral representation of Q_{cell} (eq. 79) to the sum (eq. 80) may be accomplished by taking \tilde{V}_Ω to be equal to the single effective cell pair interaction potential $\tilde{V}_{ij}^{(2)}$, defined by:

$$\begin{aligned} \tilde{V}_{ij}^{(2)}(\xi_i, \xi_j) &= 0 \quad (\text{if } \xi_i \text{ or } \xi_j = 0) \\ \exp \left\{ - \frac{1}{kT} \tilde{V}_{ij}^{(2)}(\xi_i, \xi_j) \right\} \\ &= \frac{1}{\omega^2} \int_{\omega_i} d^3\mathbf{r}_i \int_{\omega_j} d^3\mathbf{r}_j \exp \left\{ - \frac{1}{kT} V_{\gamma\delta}(r_{ij}) \right\} \quad (81) \\ &\quad (\text{if neither } \xi_i \text{ nor } \xi_j = 0) \end{aligned}$$

Clearly the former small- ω definition of \tilde{V}_Ω , at least for this two-ion case, is obtained as the limit of the more general expression (eq. 81) as ω passes to zero. The subscripts on $\tilde{V}_{ij}^{(2)}$ are intended to identify the two cells to which it refers. This effective cell pair potential will be somewhat temperature dependent.

If the system contained more than just one pair of occupied cells, and if these distinct pairs were sufficiently far from one another not to interfere, \tilde{V}_Ω , the total effective cell potential, could be built up of a sum of the individual $\tilde{V}_{ij}^{(2)}(\xi_i, \xi_j)$:

$$\tilde{V}_\Omega(\xi_1 \dots \xi_\Omega) = \sum_{i < j = 1}^{\Omega} \tilde{V}_{ij}^{(2)}(\xi_i, \xi_j) \quad (82)$$

It is attractive to suppose that \tilde{V}_Ω is always adequately represented by such a sum of cell pair effective potentials, in complete analogy with the original ion interactions themselves. Of course this cannot be rigorously true; \tilde{V}_Ω should strictly include corrections, $\tilde{V}_{ijk}^{(3)}(\xi_i, \xi_j, \xi_k)$ for simultaneous occupation of three cells (if all three ξ 's are nonzero):

$$\begin{aligned} \exp \left\{ -\frac{1}{kT} [\tilde{V}_{ij}^{(2)}(\xi_i, \xi_j) + \tilde{V}_{ik}^{(2)}(\xi_i, \xi_k) + \tilde{V}_{jk}^{(2)}(\xi_j, \xi_k) \right. \\ \left. + \tilde{V}_{ijk}^{(3)}(\xi_i, \xi_j, \xi_k)] \right\} = \frac{1}{\omega^3} \int_{\omega_i} d^3\mathbf{r}_i \int_{\omega_j} d^3\mathbf{r}_j \int_{\omega_k} d^3\mathbf{r}_k \\ \times \exp \left\{ -\frac{1}{kT} [V_{\gamma\delta}(r_{ij}) + V_{\gamma\epsilon}(r_{ik}) + V_{\delta\epsilon}(r_{jk})] \right\} \quad (83) \end{aligned}$$

by ions of types γ , δ , and ϵ , respectively; corrections for four and more cells would be similarly defined. However, we shall neglect these many-cell interaction quantities for the present purposes, and assume, therefore, that equation 82 provides an adequate expression for \tilde{V}_Ω .

The definition (eq. 81) of $\tilde{V}_{ij}^{(2)}$ permits one to get a qualitative idea of the relation of this cell pair function to its ion pair precursor, $V_{\gamma\delta}$. If the cells ω_i and ω_j are far apart, \tilde{V}_{ij} represents an average only of the very slowly varying Coulomb potential between ions of type γ and δ . Consequently, \tilde{V}_{ij} can differ only insignificantly from this Coulomb potential at large distances. On the other hand, when ω_i and ω_j are relatively near neighbors, not only does the ion Coulomb potential vary considerably across these cells, but the shorter-ranged ion interactions come into play as well. Therefore, at small distances,

$\tilde{V}_{ij}^{(2)}$ will probably exhibit deviation from the pure Coulombic inverse distance dependence. For a pure symmetrical electrolyte to which we shall restrict attention in the remainder of this section, $\tilde{V}_{ij}^{(2)}$ may thus be written as the asymptotic Coulomb term, plus a function of the cell-cell separation r_{ij} , which decays rapidly to zero with increasing r_{ij} :

$$\tilde{V}_{ij}^{(2)}(\xi_i, \xi_j) = \frac{\xi_i \xi_j (ze)^2}{Dr_{ij}} + \eta(r_{ij}; \xi_i, \xi_j) \quad (84)$$

The distances r_{ij} are to be interpreted as the distance between cell centers. The short-range cell interaction η vanishes if either ξ_i or ξ_j is zero. As the leading term in equation 84 indicates, the electrostatic charge on the ions of the symmetrical salt is $\pm ze$ (z a small integer, which, for example, would be $+1$ for NaCl, $+2$ for BaO).

The cell potential $\tilde{V}_\Omega(\xi_1 \dots \xi_\Omega)$ serves to define a normalized probability, $P_{\text{cell}}(\xi_1 \dots \xi_\Omega)$, which is the lattice theory analog of the complete Gibbs phase space distribution function, $P^{(N)}(\mathbf{r}_1 \dots \mathbf{p}_N)$, defined originally for the molten salt in equation 24

$$P_{\text{cell}}(\xi_1 \dots \xi_\Omega) = \frac{1}{Q_{\text{cell}}} \prod_{\alpha=1}^{\mu} \left(\frac{\omega}{\lambda_\alpha^3} \right)^{N_\alpha} \exp \left\{ - \frac{1}{kT} \tilde{V}_\Omega(\xi_1 \dots \xi_\Omega) \right\} \quad (85)$$

For the pure symmetrical electrolyte consisting of equal numbers of cationic and anionic particles, the number of species μ is obviously two. P_{cell} specifies much less information about the detailed state of the ionic assembly than does $P^{(N)}$, for through the ξ 's it can tell only which cells are occupied by anions or cations, but not where in these cells the ions are located, or what their momenta are. For this reason, P_{cell} is a spatially coarse-grained version of the configuration part of $P^{(N)}$.

In exactly the same way that $P^{(N)}$ led to definition of the ionic correlation functions $g^{(n)}$ (eq. 32) by integration, P_{cell} may be used to define lattice theory correlation functions, $\gamma^{(n)}$, by summation, which give the probability that the n cells whose centers are at $\mathbf{r}_1 \dots \mathbf{r}_n$ are simultaneously characterized by occupation parameters $\xi_1 \dots \xi_n$:

$$\left(\prod_{i=1}^n x_{\xi_i} \right) \gamma_{\xi_1 \dots \xi_n}^{(n)}(\mathbf{r}_1 \dots \mathbf{r}_n) = \sum_{\{\xi_j\}}'' P_{\text{cell}}(\xi_1 \dots \xi_\Omega) \quad (86)$$

The doubly primed summation is to include all sets $\{\xi_j\}$ of occupation parameters which not only are consistent with the fixed total number of ions and vacancies as before, but which have the fixed values $\xi_1 \dots \xi_n$ for the chosen set of cells. The "cell fractions" x_{ξ_i} are the fixed fractions of the total number of cells which are occupied by cations (x_+), anions (x_-) or are unoccupied (x_0),

$$x_+ + x_- + x_0 = 1 \quad (87)$$

For the chosen symmetrical electrolyte,

$$\begin{aligned} x_+ = x_- &= \frac{N}{2\Omega} = x \\ x_0 &= 1 - 2x \end{aligned} \quad (88)$$

The reason for introducing the cell fractions in equation 86, by analogy with $g^{(n)}$, is to normalize each $\gamma^{(n)}$ to unity when all chosen n cells are far from one another. On account of the relation of P_{cell} to $P^{(n)}$, $\gamma^{(n)}$ for a set of n occupied cells represents a spatially coarse-grained n th-order ion correlation function, $g^{(n)}$.

As in the case of $g^{(2)}$ in the uncellularized fundamentals of molten salt statistical theory outlined in Section IV, the lattice theory's pair correlation function, $\gamma^{(2)}$, plays a central role in the present considerations. We shall not record here each lattice theory version of the thermodynamic quantities previously adduced with $g^{(2)}$ in Section IV, except that for the energy. In principle, a knowledge of this energy at all temperatures and densities should allow deduction of the remaining thermodynamic functions by means of identities 26–28. The average energy (beyond the Born cavity energy) of the molten salt, per cell, is composed, as usual, of kinetic and potential energy contributions. The former is just $3/2 kT$ times the average number of particles in a cell ($2x$). The latter may be obtained from temperature differentiation (see eq. 26) of Q_{cell} given by equation 80, since this latter provides the interaction contribution to the Helmholtz free energy measured from the sum of Born cavity energies. Using the pairwise additive approximation for \tilde{V}_{Ω} , and referring to definition 86 for the cell pair correlation functions, one finally obtains the symmetrical salt result:

$$\begin{aligned}
& \frac{1}{\Omega} \left\{ E - \frac{N}{2} \sum_{\alpha=+,-} \left[U_{bc}^{(\alpha)} + \left(\frac{\partial U_{bc}^{(\alpha)}}{\partial(1/kT)} \right)_{\mathbf{v}} \right] \right\} \\
& = (3x)kT + \frac{x^2}{2} \sum_{\xi_i, \xi_j} \sum_{\mathbf{r}_{ij}} \left[\tilde{V}_{ij}^{(2)}(\xi_i, \xi_j) + \left(\frac{1}{kT} \right) \right. \\
& \quad \left. \times \left(\frac{\partial \tilde{V}_{ij}^{(2)}(\xi_i, \xi_j)}{\partial(1/kT)} \right)_{\mathbf{v}} \right] \gamma_{\xi_i \xi_j}^{(2)}(\mathbf{r}_{ij}) \quad (89)
\end{aligned}$$

Here, ξ_i and ξ_j are summed over the three permissible values $-1, 0$, and $+1$, and \mathbf{r}_{ij} takes on all values of the distance between the center of a specified cell (i) and the other $\Omega - 1$ cell centers.

We turn now to the central problem of the molten salt lattice theory, the determination of the cell pair correlation functions $\gamma_{\xi_i \xi_j}^{(2)}(\mathbf{r}_{ij})$. It will be convenient to abbreviate the content of cells by $+, 0, -$, for cations, vacancies, and anions, respectively. Even for the pure symmetrical salt, there are six different correlation functions,

$$\gamma_{++}^{(2)}(\mathbf{r}), \gamma_{+-}^{(2)}(\mathbf{r}), \gamma_{--}^{(2)}(\mathbf{r}), \gamma_{+0}^{(2)}(\mathbf{r}), \gamma_{-0}^{(2)}(\mathbf{r}), \gamma_{00}^{(2)}(\mathbf{r}) \quad (90)$$

There is naturally irrelevance regarding subscript order.

The restraint of no greater than single occupancy in the lattice theory implies simple linear relations between these quantities. A cell chosen at distance \mathbf{r} from another cell, whose content is known, *must* have one of the three states $+, 0, -$; since the specified cell itself may be in any of these three states of occupation, we arrive at the three conditions:

$$\begin{aligned}
1 &= x\gamma_{++}^{(2)}(\mathbf{r}) + (1 - 2x)\gamma_{+0}^{(2)}(\mathbf{r}) + x\gamma_{+-}^{(2)}(\mathbf{r}) \\
1 &= x\gamma_{0+}^{(2)}(\mathbf{r}) + (1 - 2x)\gamma_{00}^{(2)}(\mathbf{r}) + x\gamma_{0-}^{(2)}(\mathbf{r}) \\
1 &= x\gamma_{-+}^{(2)}(\mathbf{r}) + (1 - 2x)\gamma_{-0}^{(2)}(\mathbf{r}) + x\gamma_{--}^{(2)}(\mathbf{r})
\end{aligned} \quad (91)$$

By use of these relations, only three independent quantities remain from the original set (eq. 90).

Although the general ideas of the lattice theory do not demand it, a considerable economy of notation results if one can suppose that all ions, regardless of charge, interact through the same averaged cell short-range interaction η ; thus, we shall tentatively assume:

$$\eta(\mathbf{r}; \xi_i, \xi_j) = \eta(\mathbf{r}; |\xi_i|, |\xi_j|) \quad (92)$$

In this event, the lattice model becomes entirely charge-symmetric, so that as far as the correlation functions are concerned, nothing can distinguish + from - on an absolute basis. As a result, there must be the following identities:

$$\begin{aligned}\gamma_{++}^{(2)}(\mathbf{r}) &= \gamma_{--}^{(2)}(\mathbf{r}) \\ \gamma_{+0}^{(2)}(\mathbf{r}) &= \gamma_{-0}^{(2)}(\mathbf{r})\end{aligned}\tag{93}$$

Since the five equations 91 and 93 together constitute only four independent relations, there remain two independent cell pair correlation functions.

If it is the ion core repulsive forces primarily which determine the cell short-range function, η , then the subclass of symmetric salts containing KF, CsCl, and BaO should conform rather closely to the simplified lattice theory as outlined here. For these salts have very nearly equal anion and cation radii, and the definition of η (eqs. 81 and 84) should lead to minimal dependence on particle charge.*

If a large pressure were applied to the molten salt, it would presumably be possible to squeeze out the vacant cells, so each cell would contain a single ion. Under this condition, the total correlation, $\gamma_m(\mathbf{r})$, of ions of either size about a given (occupied) cell, which is the average of $\gamma_{++}^{(2)}(\mathbf{r})$ and $\gamma_{+-}^{(2)}(\mathbf{r})$,

$$\gamma_m(\mathbf{r}) = 1/2[\gamma_{++}^{(2)}(\mathbf{r}) + \gamma_{+-}^{(2)}(\mathbf{r})]\tag{94}$$

is everywhere unity. Thus, though about a central cell we should generally expect that shells of neighboring cells would contain varying compositions, the resultant fluctuations in $\gamma_{++}^{(2)}$ and $\gamma_{+-}^{(2)}$ in equation 94 completely cancel one another. The extreme case of this cancellation would be encountered in the case of a perfectly ordered crystal, with cells centered about the lattice positions, for then concentric shells would be *entirely* one species or the other, but γ_m is still identically unity.

In the ordinary liquid range, there will, however, exist a certain fraction, $1 - 2x$, of empty cells. In this case the cancellation inherent in the definition of γ_m will not be quite complete. But for

* It should be pointed out in this connection that a choice of cells, as in one of the close-packed arrays, produces individual cells which are nearly spherical. An average of the Coulomb potential over a spherical region is, of course, equal to the Coulomb potential at the center of this region, so the electrostatic contribution to η will in any event be small for these compact cells.

fairly large cell center pair distances \mathbf{r} , where it is essentially the electrostatic interactions alone which determine the occupation probabilities, a certain amount of cancellation still can be anticipated. Thus, for a given \mathbf{r} , a like ion pair might experience a net positive mean electrostatic interaction (and hence less such pairs would be found at this distance than on a random basis), but an unlike pair would exhibit enhanced probability by virtue of charge sign change, with resultant average interaction sign change. As a consequence, the mean cell pair correlation function γ_m is expected to attain its asymptotic value unity, as \mathbf{r} increases, much more rapidly than do either $\gamma_{++}^{(2)}$ or $\gamma_{+-}^{(2)}$.

On the other hand, the ratio of $\gamma_{++}^{(2)}$ to $\gamma_{+-}^{(2)}$ will fluctuate as \mathbf{r} increases with even greater amplitude than either its numerator or denominator, since as already acknowledged, when one is small relative to unity, the other should be large. Therefore, if a function $\bar{\varphi}$ is defined by the relation,

$$\exp \left\{ - \frac{2(ze)^2 \bar{\varphi}(\mathbf{r})}{DkT} \right\} = \frac{\gamma_{++}^{(2)}(\mathbf{r})}{\gamma_{+-}^{(2)}(\mathbf{r})} \quad (95)$$

the behavior of this new quantity should alone be virtually sufficient to characterize the order imposed upon the liquid assembly of ions attributable to their electrostatic charges.

Equations 94 and 95 may be solved simultaneously to yield:

$$\begin{aligned} \gamma_{++}^{(2)}(\mathbf{r}) &= \frac{2\gamma_m(\mathbf{r})}{\exp \left\{ \frac{2(ze)^2 \bar{\varphi}(\mathbf{r})}{DkT} \right\} + 1} \\ &\sim 1 - \frac{(ze)^2 \bar{\varphi}(\mathbf{r})}{DkT} \quad (\text{large } |\mathbf{r}|) \end{aligned} \quad (96)$$

$$\begin{aligned} \gamma_{+-}^{(2)}(\mathbf{r}) &= \frac{2\gamma_m(\mathbf{r}) \exp \left\{ \frac{2(ze)^2 \bar{\varphi}(\mathbf{r})}{DkT} \right\}}{\exp \left\{ \frac{2(ze)^2 \bar{\varphi}(\mathbf{r})}{DkT} \right\} + 1} \\ &\sim 1 + \frac{(ze)^2 \bar{\varphi}(\mathbf{r})}{DkT} \quad (\text{large } |\mathbf{r}|) \end{aligned} \quad (97)$$

The asymptotic behaviors follow immediately from the long-range decay character of $\bar{\varphi}(\mathbf{r})$ vs. $\gamma_m(\mathbf{r})$. Utilizing next the normalization and charge symmetry conditions eqs. 91 and 93, the remaining cell correlation functions must in turn be expressible in terms of the fundamental quantities γ_m and $\bar{\varphi}$. Interestingly, the latter does not appear:

$$\begin{aligned}\gamma_{+0}^{(2)}(\mathbf{r}) &= 1 - \frac{2x}{1-2x} [\gamma_m(\mathbf{r}) - 1] \\ \gamma_{00}^{(2)}(\mathbf{r}) &= 1 + \frac{4x^2}{(1-2x)^2} [\gamma_m(\mathbf{r}) - 1]\end{aligned}\tag{98}$$

That only γ_m is involved is consistent with the fact that an uncharged vacant cell should not be subject directly to electrostatic correlation.

A variable λ is now introduced (analogous to the similar parameter in eq. 50), which has the effect of allowing continuous variation of the electrostatic charge on an ion contained in a given cell (identified arbitrarily as cell 1). The "physical" value of the charge, $\xi_1 ze$, is thus replaced formally by $\lambda \xi_1 ze$. As λ varies continuously between -1 and $+1$, when this cell 1 contains an ion, the effect is to change this ion from a cation to an anion, or vice versa. Setting $\lambda = 0$ discharges the ion electrostatically, so it may interact with its neighbors only through the short-range cell interaction, $\eta(\mathbf{r})$. This discharged ion core then appears to act very much like a dissolved noble gas atom. For arbitrary λ , the cell potential \bar{V}_Ω must now be written:

$$\begin{aligned}\bar{V}_\Omega(\xi_1 \dots \xi_\Omega; \lambda) &= \sum_{j=2}^{\Omega} \left[\lambda \frac{\xi_1 \xi_j (ze)^2}{Dr_{1j}} + \eta(r_{1j}, |\xi_1|, |\xi_j|) \right] \\ &+ \sum_{i<j=2}^{\Omega} \left[\frac{\xi_i \xi_j (ze)^2}{Dr_{ij}} + \eta(r_{ij}, |\xi_i|, |\xi_j|) \right]\end{aligned}\tag{99}$$

Furthermore, it is this λ -dependent potential which must be used in the definition of the various $\gamma^{(n)}$ (eq. 86) for cell correlation functions of any order, when cell 1 is variably charged.

If cell 1 is vacant, obviously variations in λ can produce no observable change in the properties of the cellularized system. Specifi-

cally, the cell pair correlation functions for this empty cell and another cell with any state of occupation are independent of λ .*

$$\begin{aligned}\gamma_{0+}^{(2)}(\mathbf{r}, \lambda) &= \gamma_{0+}^{(2)}(\mathbf{r}, 1) \\ \gamma_{0-}^{(2)}(\mathbf{r}, \lambda) &= \gamma_{0-}^{(2)}(\mathbf{r}, 1) \\ \gamma_{00}^{(2)}(\mathbf{r}, \lambda) &= \gamma_{00}^{(2)}(\mathbf{r}, 1)\end{aligned}\quad (100)$$

On the other hand, if cell 1 is not vacant, the actual charge variation produces change in the corresponding $\gamma^{(2)}$'s. One can easily see, for this simple charge symmetric lattice model, the following relations are valid:

$$\begin{aligned}\gamma_{++}^{(2)}(\mathbf{r}, \lambda = -1) &= \gamma_{+-}^{(2)}(\mathbf{r}, \lambda = +1) \\ &= \gamma_{+-}^{(2)}(\mathbf{r}, \lambda = +1) = \gamma_{--}^{(2)}(\mathbf{r}, \lambda = -1)\end{aligned}\quad (101)$$

In view of definitions 94 and 95, it must be admitted that γ_m and $\bar{\varphi}$ likewise are explicitly λ -dependent, when they refer to correlations between cell pairs including cell 1;

$$\gamma_m(\mathbf{r}, \lambda) \quad \bar{\varphi}(\mathbf{r}, \lambda)$$

But by virtue once again of the charge symmetry of the simple fused salt model we are considering,

$$\begin{aligned}\gamma_m(\mathbf{r}, -\lambda) &= \gamma_m(\mathbf{r}, \lambda) \\ \bar{\varphi}_m(\mathbf{r}, -\lambda) &= -\bar{\varphi}(\mathbf{r}, \lambda)\end{aligned}\quad (102)$$

In particular, this last equality implies

$$\bar{\varphi}(\mathbf{r}, \lambda = 0) = 0 \quad (103)$$

We are now in a position to deduce a functional equation for determination of the fundamental electrostatic correlation quantity $\bar{\varphi}$. From its definition (eq. 95), for arbitrary λ , one has the identity

$$\begin{aligned}\bar{\varphi}(\mathbf{r}_{12}, \lambda) &= \frac{DkT}{2(ze)^2} \int_0^\lambda d\lambda' \\ &\times \left[\frac{\partial \log \gamma_{+-}^{(2)}(\mathbf{r}_{12}, \lambda')}{\partial \lambda'} - \frac{\partial \log \gamma_{++}^{(2)}(\mathbf{r}_{12}, \lambda')}{\partial \lambda'} \right] \quad (104)\end{aligned}$$

* Although the original $\gamma^{(2)}$'s were invariant to the subscript order, before introduction of λ , we now conventionally suppose that the first subscript refers to the species of the content of cell 1 (when $\lambda = 1$), and that the second subscript refers to the content of the cell whose center is at relative displacement \mathbf{r} from cell 1.

The two λ' derivatives may be obtained from equation 86, upon setting $n = 2$, and using a λ -dependent P_{cell} . With the aid of equation 86 again, to identify triple cell correlation functions, one finally obtains

$$\begin{aligned} \bar{\varphi}(\mathbf{r}_{12}, \lambda) = & \frac{\lambda}{r_{12}} + \frac{x}{2} \sum_{\mathbf{r}_3 (\neq \mathbf{r}_1, \mathbf{r}_2)} \int_0^\lambda d\lambda' \frac{1}{r_{13}} \left[\frac{\gamma_{+++}^{(3)}(123, \lambda')}{\gamma_{++}^{(2)}(12, \lambda')} \right. \\ & \left. - \frac{\gamma_{++-}^{(3)}(123, \lambda')}{\gamma_{+-}^{(2)}(12, \lambda')} - \frac{\gamma_{+-+}^{(3)}(123, \lambda')}{\gamma_{+-}^{(2)}(12, \lambda')} + \frac{\gamma_{+--}^{(3)}(123, \lambda')}{\gamma_{+-}^{(2)}(12, \lambda')} \right] \quad (105) \\ (123) = & (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \end{aligned}$$

The summation over cell centers \mathbf{r}_3 is to include all cells of the system with the exception of the chosen pair (at \mathbf{r}_1 and \mathbf{r}_2) for which $\bar{\varphi}$ is to be evaluated.

The central quantity $\bar{\varphi}$ obviously has two contributions, as may be seen from equation 105. The first, λ/r_{12} , represents precisely the correlation in content between cells 1 and 2, as a result of the direct Coulomb interaction between these cells. The second is provided by the integral term in equation 105, and is the modification ("shielding") of the direct interaction between 1 and 2 by the variable distribution of ions and vacancies among cells surrounding 1 and 2.

Having once adopted the total cell-space interaction energy \bar{V}_Ω in form 99, the functional equation 105 for $\bar{\varphi}$ follows as a rigorous consequence. Its immediate utility, though, is limited by the fact that it contains the yet undetermined $\gamma^{(3)}$'s. However, a plausible set of approximations for the $\gamma^{(3)}$ may be proposed by which equation 105 will lead to a determinate equation for $\bar{\varphi}$. We postulate

$$\begin{aligned} \gamma_{\alpha\beta\delta}^{(3)}(123, \lambda') \cong & \gamma_{\alpha\beta}^{(2)}(12, \lambda') + \gamma_{\alpha\delta}^{(2)}(13, \lambda') + \\ & \gamma_{\beta\delta}^{(2)}(23) - 2 \quad (106) \\ \alpha, \beta, \delta = & +, 0, - \end{aligned}$$

Here, $\gamma_{\beta\delta}^{(2)}(23)$ refers to an assembly in which λ has been set equal to its "physical" value, $+1$. This is the simplest approximation for the $\gamma^{(3)}$'s in terms of $\gamma^{(2)}$'s which not only satisfies the normalization conditions:

$$\begin{aligned} \sum_{\alpha} x_{\alpha} \gamma_{\alpha\beta\delta}^{(3)}(123, \lambda') &= \gamma_{\beta\delta}^{(2)}(23) \\ \sum_{\beta} x_{\beta} \gamma_{\alpha\beta\delta}^{(3)}(123, \lambda') &= \gamma_{\alpha\delta}^{(2)}(13, \lambda') \\ \sum_{\delta} x_{\delta} \gamma_{\alpha\beta\delta}^{(3)}(123, \lambda') &= \gamma_{\alpha\beta}^{(2)}(12, \lambda') \end{aligned} \quad (107)$$

(these are the generalization to the $\gamma^{(3)}$ case of conditions 91), but additionally reduces to the proper $\gamma^{(2)}$ when one cell of the triplet is sufficiently far from the other two to be randomly occupied. It may be shown (67), furthermore, that equation 106 is exact if the number of vacant cells is negligibly small ($x = 1/2$). A reduction of the triplet correlation functions to a linear combination of pair functions, rather than a product of the three pair functions [the Kirkwood superposition approximation (40)] which fails to satisfy equations 107, thus seems more appropriate in this lattice theory.

When approximation 106 is used to eliminate the triplet cell correlation functions from the $\bar{\varphi}$ equation, this latter is found to be expressible solely in terms of this unknown function itself, as well as the mean correlation function, γ_m :

$$\begin{aligned} \bar{\varphi}(12, \lambda) = & \frac{1}{r_{12}} \left\{ \lambda + x \int_0^\lambda d\lambda' \left[\cosh \left(\frac{2(ze)^2 \bar{\varphi}(12, \lambda')}{DkT} \right) - 1 \right] \right\} \\ & + \frac{D}{2(ze)^2} \int_0^\lambda d\lambda' \frac{\epsilon_c(\lambda')}{\lambda' \gamma_m(12, \lambda')} \sinh \left[\frac{2(ze)^2 \bar{\varphi}(12, \lambda')}{DkT} \right] \\ & - x \left\{ \int_0^\lambda d\lambda' \frac{1 + \cosh [2(ze)^2 \bar{\varphi}(12, \lambda') / DkT]}{\gamma_m(12, \lambda')} \right\} \\ & \times \sum_{r_3 (\neq r_1, r_2)} \frac{\gamma_m(23)}{r_{13}} \tanh \left[\frac{(ze)^2 \bar{\varphi}(23)}{DkT} \right] \quad (108) \end{aligned}$$

Once again, functions without explicit appearance of λ as an argument are to be taken at $\lambda = +1$. The position-independent quantity $\epsilon_c(\lambda)$ is the purely Coulombic part of the average interaction energy of a partially charged cation with its surroundings:

$$\epsilon_c(\lambda) = - \frac{2(ze)^2 x \lambda}{D} \sum_{r_3 (\neq r_1)} \frac{\gamma_m(13, \lambda)}{r_{13}} \tanh \left[\frac{(ze)^2 \bar{\varphi}(13, \lambda)}{DkT} \right] \quad (109)$$

The $\bar{\varphi}$ equation 108, even now that triple cell correlations have been eliminated, is still unwieldy. First, it is nonlinear in the desired $\bar{\varphi}$; and second, γ_m is not precisely known. In the interests of obtaining an explicit, albeit approximate, solution for $\bar{\varphi}$, we shall choose to circumvent these barriers by supposing that $\bar{\varphi}$ is sufficiently small that equation 108 may be linearized with respect to it, and that γ_m is identically unity (as it is when no vacant cells are present). This latter assumption is equivalent to supposing that vacant cells are

randomly mixed among the entire set of cells. When these simplifications are employed, equation 108 reduces to

$$\bar{\varphi}(\mathbf{r}_{12}) = \frac{1}{r_{12}} - \frac{\kappa^2 \omega}{4\pi} \sum_{\mathbf{r}_3 (\neq \mathbf{r}_1, \mathbf{r}_2)} \frac{1}{r_{13}} \bar{\varphi}(\mathbf{r}_{23}) \quad (110)$$

where λ has been set equal to +1 to correspond to the fully coupled ion set. The Debye-Hückel parameter for the symmetrical salt has been introduced:

$$\kappa^2 = \frac{8\pi x(ze)^2}{DkT\omega} \quad (111)$$

Once solution for $\bar{\varphi}$ has been effected in this $\lambda = +1$ case, the result may be utilized in solving analogously the arbitrary λ equation, obtained from equation 108 by the same approximations as was 110; we shall not dwell on this slight procedural generalization.

The positional summation restriction on \mathbf{r}_3 in the linear equation 110 may be removed by defining a function $l(\mathbf{r})$ equal, at all relative cell center positions \mathbf{r} , to r^{-1} , except when $\mathbf{r} = 0$:

$$\begin{aligned} l(\mathbf{r}) &= \frac{1}{r} & |\mathbf{r}| \neq 0 \\ &= 0 & |\mathbf{r}| = 0 \end{aligned} \quad (112)$$

Therefore,

$$\begin{aligned} \bar{\varphi}(\mathbf{r}_{12}) &= (1 + \zeta)l(\mathbf{r}_{12}) - \frac{\kappa^2 \omega}{4\pi} \sum_{\mathbf{r}_3} l(\mathbf{r}_{13}) \bar{\varphi}(\mathbf{r}_{23}) \\ \zeta &= \frac{\kappa^2 \omega}{4\pi} \bar{\varphi}(0) \end{aligned} \quad (113)$$

The constant ζ is arbitrary so far as equation 113 is concerned. Mathematically, a solution exists for every ζ . But physically, a single value of ζ must eventually be chosen to yield a unique $\bar{\varphi}$ which satisfies a local electroneutrality condition. This latter demands that the total average electrostatic charge surrounding an occupied central cell must precisely counterbalance (and hence completely shield) that central cell's charge. The precise statement of this condition in terms of γ_m and $\bar{\varphi}$ is easily found to be

$$\frac{1}{2x} = \sum_{\mathbf{r} \neq 0} \gamma_m(\mathbf{r}) \tanh \left[\frac{(ze)^2 \bar{\varphi}(\mathbf{r})}{DkT} \right] \quad (114)$$

which may be obtained from expression of the average ionic (and hence charge) densities near an occupied cell in terms of the individual $\gamma^{(2)}$'s.

The set of cells spanning the molten salt volume has been chosen so that their centers form a regular lattice. This lattice of centers may be regarded as a reciprocal lattice for a certain unit cell τ (the first Brillouin zone for the \mathbf{r} lattice) in the three-dimensional space of vectors, \mathbf{k} . τ is completely specified as usual by the conditions (12): (a) τ and its periodicity images completely fill \mathbf{k} space ($\mathbf{k} = 0$ is taken as the center of τ); (b) if \mathbf{k}_{ij} is a vector connecting equivalent points of two such \mathbf{k} space cells τ_i and τ_j , then

$$\exp [i\mathbf{r} \cdot \mathbf{k}_{ij}] = 1$$

for all members \mathbf{r} of the original lattice of centers; (c) τ 's circumscribed sphere is a minimum.

The general solution to linear equation 113 may now be accomplished by a Fourier transform method. For any function $f(\mathbf{r})$ defined on the lattice of cell centers \mathbf{r} , we have the following simultaneous pair of equations:

$$\begin{aligned} F(\mathbf{k}) &= \sum_{\mathbf{r}} \exp [i\mathbf{k} \cdot \mathbf{r}] f(\mathbf{r}) \\ f(\mathbf{r}) &= \frac{1}{\tau} \int_{\tau} \exp [-i\mathbf{r} \cdot \mathbf{k}] F(\mathbf{k}) d^3\mathbf{k} \end{aligned} \quad (115)$$

These are the adaptation, to present circumstances, of the Fourier integral identities in three dimensions (61), which would be obtained for an infinitely dense set of positions \mathbf{r} .

Applying the summation operation of the first of equations 115 to both sides of 113, solving the resultant algebraic equation for the transform of $\bar{\varphi}$, then finally inverting by means of the second of equations 115, the desired solution is obtained in the form:

$$\begin{aligned} \bar{\varphi}(\mathbf{r}) &= \frac{1 + \zeta}{\tau} \int_{\tau} \frac{L(\mathbf{k}) \exp [-i\mathbf{r} \cdot \mathbf{k}]}{1 + \frac{\kappa^2 \omega}{4\pi} L(\mathbf{k})} d^3\mathbf{k} \\ L(\mathbf{k}) &= \sum_{\mathbf{r}} \exp [i\mathbf{k} \cdot \mathbf{r}] l(\mathbf{r}) \end{aligned} \quad (116)$$

This last summation must be carefully performed; to avoid divergence, it is sufficient to place in the summand an extra convergence factor $\exp(-\alpha r)$, then after (the now uniformly convergent) summation is accomplished, allow α to approach zero.

The sum $L(\mathbf{k})$ generally cannot be put into closed form. However, it may be closely approximated by an integral which can explicitly be carried out. For this reason, we shall replace $L(\mathbf{k})$ by an integral of $\exp[i\mathbf{k}\cdot\mathbf{r}]/r$, which is the value of the summand in equation 116 at all lattice points except the origin, outside of a sphere of volume

$$\omega = \frac{4\pi}{3} r_0^3$$

equal to the volume of the central cell (for which l vanishes).

$$\begin{aligned} L(\mathbf{k}) &\cong \frac{1}{\omega} \lim_{\alpha \rightarrow 0} \int_{|\mathbf{r}| \geq r_0} d^3\mathbf{r} \frac{\exp[i\mathbf{k}\cdot\mathbf{r} - \alpha r]}{r} \\ &= \frac{4\pi}{k^2\omega} \cos(kr_0) \end{aligned} \quad (117)$$

Sphericalization of the original unit cell is not at all a drastic modification if the original lattice were one of the close-packed structures, for cells in those cases are already nearly spherical.

In the inversion integral (eq. 116), the reciprocal space unit cell τ likewise is sphericalized, maintaining its volume

$$\tau = (2\pi)^3/\omega$$

Use of this last simplification finally permits the desired $\bar{\varphi}(\mathbf{r})$ to be expressed as a simple quadrature:

$$\begin{aligned} \bar{\varphi}(\mathbf{r}) &= \frac{\zeta'}{(r/r_0)} \int_0^c dl \frac{l \cos l \sin [(r/r_0)l]}{l^2 + (\kappa r_0)^2 \cos l} \\ c &= (9\pi/2)^{1/3} = 2.418 \end{aligned} \quad (118)$$

ζ' is once again an arbitrary multiplicative constant whose value must be chosen to satisfy the local electroneutrality condition (eq. 114).

For molten salts near their normal melting points, $(\kappa r_0)^2$ is around 100. With these values, the denominator in integral 118 will have a simple root at

$$l_0 \cong \frac{\pi}{2} + \left(\frac{\pi}{2\kappa r_0}\right)^2 \quad (119)$$

The large typical values of κr_0 , for which this is an asymptotic estimate, yield a root l_0 well within the interval of integration of equation 118. In this situation, it is necessary to specify the sense of integration across this pole in the complex l plane. In the following section on the theory of the complete (uncellularized) pair correlation function, we shall see by analogy that the appropriate interpretation is such to remove the long-range contributions to $\bar{\varphi}$ arising from this singularity. The analogy leads one to rewrite 118 in the form:

$$\bar{\varphi}(\mathbf{r}) = \frac{i\zeta'}{2(r/r_0)} \int_{-c}^{+c} dl \frac{l \cos l \exp [-i(r/r_0)l]}{l^2 + (\kappa r_0)^2 \cos l} \quad (120)$$

where the contour is to be deformed *below* the real axis at the two singularities of the integrand at $\pm l_0$, as shown in Figure 9. In form 120, $\sin [(r/r_0)l]$ in equation 118 has been converted to its exponential representation. Alternatively, the two infinitesimal portions of the contour at $\pm l_0$ may explicitly be integrated to leave a Cauchy principle value integral (CPV):

$$\bar{\varphi}(\mathbf{r}) = \frac{\zeta'}{(r/r_0)} \left\{ \frac{\pi l_0 \cos l_0 \cos [(r/r_0)l_0]}{2l_0 - (\kappa r_0)^2 \sin l_0} + \int_0^c dl \frac{l \cos l \sin [(r/r_0)l]}{l^2 + (\kappa r_0)^2 \cos l} \right\} \quad (\text{CPV}) \quad (121)$$

In view of the several approximations used in derivation of formula 121, or its equivalent (eq. 120), it can only be regarded as a rather crude estimate of $\bar{\varphi}$. It should ultimately prove useful, though, as a first step in iterative schemes designed to construct self-consistent solutions to the more exact nonlinear sum (eq. 108). In any event, it will provide a qualitatively instructive expression for $\bar{\varphi}$.

Even without having to perform explicit numerical integration of equation 120 or 121, the gross character of $\bar{\varphi}$ may be deduced. Aside from the sine factor, the integrand of equation 121 is positive over virtually the entire range of integration; the sine factor, however, implies then that the integral oscillates as r increases, and $\bar{\varphi}$ approaches zero for large r . This behavior is exhibited schematically in Figure 10.

Referring to definitions 96 and 97, and remembering that γ_m has been treated as identically unity for $|\mathbf{r}| > 0$, we see that this simple calculation predicts alternating shells of anionic and cationic cells around a central occupied cell. Since the distance between successive

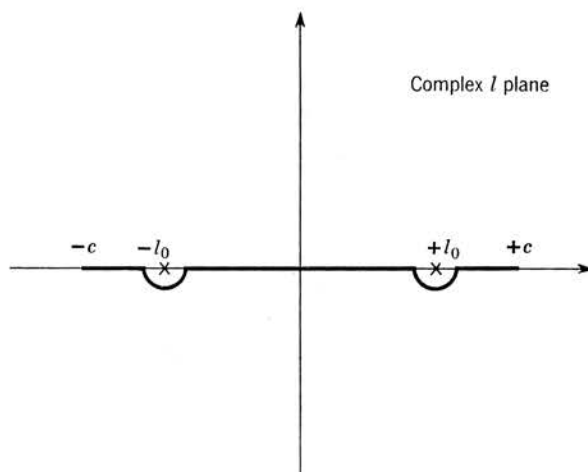


Fig. 9. Integration contour employed in equation 120 of the molten salt lattice theory. Crosses on the real axis indicate positions of the roots of $l^2 + (\kappa r_0)^2 \times \cos l = 0$ just below which the integration must be deformed into the lower half complex plane.

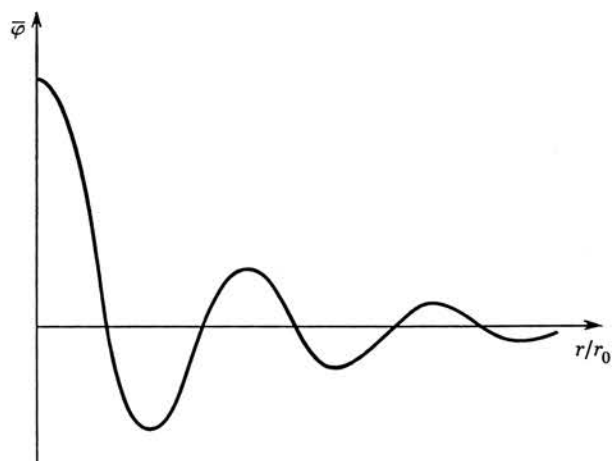


Fig. 10. Qualitative behavior of the lattice theory's electrostatic correlation quantity, $\bar{\varphi}$.

crests and troughs of $\bar{\varphi}$ is indicated by 121 to be comparable to r_0 , it is predicted that dense molten electrolytes have ions arranged on the average in much the same way as do the corresponding crystalline solids, where also successive shells of neighbors differ in charge sign. Of course, there is much more disorder in the liquid state which amounts in the lattice theory not only to the larger number of vacancies, many of which are introduced on melting, but probably as well to less complete "sorting" of ions in the successive shells. It is nevertheless interesting that the salt can take advantage of a rudimentary solid-like alternation of anions and cations to lower its electrostatic energy. It is characteristic of such vestigial order in liquids to appear in the distribution of particle pairs rather than as long-range order in the solid-state sense of average single-particle-center density regularity.

Although this rough computation of $\bar{\varphi}$ on a lattice theory basis is not sufficient to demonstrate the fact,* the persistence of order (in cell pair space) outward from a central cell is much less in liquids than in the strongly ordered crystal. This behavior is more aptly discussed in the complete pair correlation function theory, and will therefore be analyzed in the next section.

At sufficiently high temperatures, κr_0 becomes small enough that the integrand of equation 118 has no pole in the interval of integration. In this limit, it is easy to show that $\bar{\varphi}$ is equal to

$$\bar{\varphi}(r) = A \frac{\exp(-\kappa r)}{r} \quad (122)$$

so that this lattice theory properly produces the Debye-Hückel description of electrolytes in the appropriate limits ($T \rightarrow \infty$, or $x \rightarrow 0$).

VI. Properties of the Complete Ionic Pair Correlation Functions

The preceding lattice theory is interesting in that it can predict rather easily at least the dominant characteristics of the microscopic structure of fused salts. In fact, many of the lattice theory ideas can be freed from the special requirements of that theory, and applied with little modification to analysis of the more informative particle (rather than cell) correlation functions, $g_{\alpha\beta}^{(2)}$.

* Presumably a self-consistent solution to the complete nonlinear equation 108 would be more accurate in this regard.

In the demanding regime of exact properties of the $g_{\alpha\beta}^{(2)}$, it has not yet been possible to adduce rigorous relations by which these fundamental quantities may be precisely determined. Nevertheless, the partial information which is available from approximate formulation of the theory is helpful in supporting the general picture of molten salt ionic arrangement. Additionally, the approximate analysis should be amenable to reasonably accurate numerical solution, at least for simple salts, and it points out as well what information is still required to attain exact solution.

On account of the resulting compactness of notation, we will restrict attention initially to the elementary class of monatomic salts (KF, CsCl, BaO) which are not only charge symmetric, but which can also be regarded as displaying identical ion core forces between all ion pairs (equal ion sizes). Generalization to description of less regular salts will be suggested by the specialized theory, and its requirements will be outlined briefly later.

In the same manner as in the lattice theory, it proves useful to introduce a continuously variable charging parameter λ , attached now to a specific ion, ion 1, rather than to a specific cell. For the elementary salt model, there are only two independent ion pair correlation functions, involving this electrostatically partially coupled ion (we assume $\lambda = +1$ produces a fully charged cation, $\lambda = -1$ an anion); they are $g_{++}^{(2)}(r, \lambda)$ and $g_{+-}^{(2)}(r, \lambda)$. Following the lead of the cruder lattice theory, we define a mean correlation function, $g_m(r, \lambda)$, and an electrostatic correlation quantity, $\varphi(r, \lambda)$, by the relations:

$$g_m(r, \lambda) = 1/2[g_{++}^{(2)}(r, \lambda) + g_{+-}^{(2)}(r, \lambda)] \quad (123)$$

$$\exp\left[-\frac{2\varphi(r, \lambda)}{kT}\right] = \frac{g_{++}^{(2)}(r, \lambda)}{g_{+-}^{(2)}(r, \lambda)} \quad (124)$$

Inversely,

$$\begin{aligned} g_{++}^{(2)}(r, \lambda) &= \frac{2g_m(r, \lambda)}{\exp\left[\frac{2\varphi(r, \lambda)}{kT}\right] + 1} \\ g_{+-}^{(2)}(r, \lambda) &= \frac{2g_m(r, \lambda) \exp\left[\frac{2\varphi(r, \lambda)}{kT}\right]}{\exp\left[\frac{2\varphi(r, \lambda)}{kT}\right] + 1} \end{aligned} \quad (125)$$

It is to be expected once again that the individual fluctuations of $g_{++}^{(2)}$ and $g_{+-}^{(2)}$ about unity cancel to a large extent in g_m , as r increases, whereas they reinforce one another in φ . These fluctuations are larger than in the corresponding cell quantities under identical conditions of temperature and density; the latter, it must be remembered, represent spatial averages of ionic densities over the cell regions.

The mean correlation function g_m may be constructed in a way which shows that it is rigorously the pair correlation function acting between a partially coupled particle, and another particle in a fluid composed of $N - 2$ particles all identical with the second, and all interacting only through short-range forces. In fact, the molten salt is equivalent in all thermodynamic respects to this single-component fluid with (when $\lambda \neq 1$) a single, somewhat modified particle, the one numbered 1. The configuration integral appearing in the canonical partition function (eq. 29) includes in its region of integration all positions of the N ions within the container. Specifically, for any given set of positions $\mathbf{r}_1 \dots \mathbf{r}_N$ for the ions, all other permutations of the ions among these fixed positions are included as well. Therefore, the value of the configuration integral is necessarily unchanged, if one were to replace the integrand for a given $\mathbf{r}_1 \dots \mathbf{r}_N$, by its average over all different ways of distributing the fully coupled ions $2 \dots N$ over the sites $\mathbf{r}_2 \dots \mathbf{r}_N$ (generally not forming a regular array, of course). The ion 1 at \mathbf{r}_1 is to be exempted from this averaging procedure to retain this unusually charged particle at a fixed site.

The mean correlation function as defined by equation 123 is a straight arithmetic mean of $g_{++}^{(2)}$ and $g_{+-}^{(2)}$. Since there are essentially equal numbers of anions and cations among the $N - 1$ ions numbered $2 \dots N$, we may also take $g_m(r, \lambda)$ to be the average of all pair correlation functions between ion 1 and each of $2 \dots N$ in turn. This latter average may be written (see eq. 32):

$$g_m(r_{10}, \lambda) = \frac{\mathfrak{V}^2}{(N - 1)Z_N(\lambda)} \sum_{i=2}^N \int_{\mathfrak{V}} d^3\mathbf{r}_2 \dots \int_{\mathfrak{V}} d^3\mathbf{r}_N \delta(\mathbf{r}_i - \mathbf{r}_0) \\ \times \exp \left[- \frac{V_N(\mathbf{r}_1 \dots \mathbf{r}_N, \lambda)}{kT} \right] \quad (126)$$

$$Z_N(\lambda) = \int_{\mathfrak{V}} d^3\mathbf{r}_1 \dots \int_{\mathfrak{V}} d^3\mathbf{r}_N \exp \left[- \frac{V_N(\mathbf{r}_1 \dots \mathbf{r}_N, \lambda)}{kT} \right]$$

For each member of the sum in the first equation, the Dirac delta function constrains the corresponding ion to be at position \mathbf{r}_0 , so that the average involves only $g^{(2)}$'s with identical distance arguments.

Let N_c and N_a respectively denote the number of cations (charge $+ze$) and anions ($-ze$) among the set $2 \dots N$. We have claimed in effect that averaging

$$\exp \left[- \frac{V_N(\mathbf{r}_1 \dots \mathbf{r}_N, \lambda)}{kT} \right]$$

over all ways of assigning signs of $\xi_2 \dots \xi_N$ to the sites $\mathbf{r}_2 \dots \mathbf{r}_N$, where ion j had originally charge $\xi_j ze$, will not change the value of the integrals in equation 126. Since there are exactly $(N_a + N_c)! / N_a! N_c!$ such distinct assignments possible, a pseudopotential $\Psi_N(\mathbf{r}_1 \dots \mathbf{r}_N, \lambda, T)$ is defined by this averaging procedure:

$$\begin{aligned} & \exp \left[- \frac{1}{kT} \Psi_N(\mathbf{r}_1 \dots \mathbf{r}_N, \lambda, T) \right] \\ &= \frac{N_a! N_c!}{(N_a + N_c)!} \sum'_{\xi_2 \dots \xi_N = \pm 1} \exp \left[- \frac{1}{kT} V_N(\mathbf{r}_1 \dots \mathbf{r}_N, \xi_2 \dots \xi_N) \right] \end{aligned} \quad (127)$$

As indicated by the prime, the summation must maintain N_c ξ 's which are $+1$ and N_a ξ 's equal to -1 , among the set $\xi_2 \dots \xi_N$; aside from the insignificant variable charge λze on ion 1, this is precisely the system electroneutrality condition. With this definition, Ψ_N is clearly symmetric with respect to interchange of pairs of positions $\mathbf{r}_2 \dots \mathbf{r}_N$. Hence, the integral expression for g_m , after the integrand is averaged by equation 127, has all $N - 1$ members of the sum in equation 126 identical. Accordingly, one may write:

$$g_m(r_{12}, \lambda) = \frac{\mathcal{V}^2}{Z_N(\lambda)} \int_{\mathcal{V}} d^3\mathbf{r}_3 \dots \int_{\mathcal{V}} d^3\mathbf{r}_N \exp \left[- \frac{1}{kT} \Psi_N(\mathbf{r}_1 \dots \mathbf{r}_N, \lambda, T) \right] \quad (128)$$

$$Z_N(\lambda) = \int_{\mathcal{V}} d^3\mathbf{r}_1 \dots \int_{\mathcal{V}} d^3\mathbf{r}_N \exp \left[- \frac{1}{kT} \Psi_N(\mathbf{r}_1 \dots \mathbf{r}_N, \lambda, T) \right]$$

The configuration integral $Z_N(\lambda)$ (or equivalently the entire canonical partition function) and the mean correlation function therefore correspond to a fluid of N particles, all of which but one are identical.

For the fully coupled case, $\lambda = +1$, Ψ_N becomes completely symmetric in all its N configuration arguments, for the elementary class of salts considered, and so in this limit all N particles of the equivalent fluid are identical.

It is possible to provide at least a partial characterization of the pseudopotential Ψ_N beyond the formal definition (eq. 127). A temperature differentiation of this definition yields a differential equation for Ψ_N :

$$\frac{\partial[\Psi_N(\lambda, T)/kT]}{\partial(1/kT)} = \langle V_N(\lambda) \rangle_T \quad (129)$$

$$\langle f \rangle_T = \frac{\sum'_{\xi_2 \dots \xi_N = \pm 1} f \exp \left[-\frac{V_N(\xi_2 \dots \xi_N, \lambda)}{kT} \right]}{\sum'_{\xi_2 \dots \xi_N = \pm 1} \exp \left[-\frac{V_N(\xi_2 \dots \xi_N, \lambda)}{kT} \right]}$$

The averages, denoted by angular brackets with a temperature subscript, serve as before to distribute anions and cations 2... N in all possible ways over positions $\mathbf{r}_2 \dots \mathbf{r}_N$. Unlike the previous case in definition of Ψ_N , though, the various distributions are not equally represented, but are weighted according to the corresponding interaction via a Boltzmann factor. This present average thus is a temperature-dependent operation, and is equal to the former only as T becomes infinite.

The standard form (eq. 23) for the molten salt potential energy, V_N , contains a Born cavity energy for each particle. But since these are independent of position, they can have no effect on the arrangement of ions in the melt, and in particular do not affect the ionic pair correlation functions. In the considerations of this section, therefore, it is convenient to disregard the total Born cavity energy, and so to suppose that the zero of energy is chosen to make V_N a sum only of the remaining particle pair potentials:

$$V_N(\lambda) = V_N^{(s)} + \frac{(ze)^2}{D} \left\{ \sum_{j=2}^N \frac{\lambda \xi_j}{r_{1j}} + \sum_{i < j=2}^N \frac{\xi_i \xi_j}{r_{ij}} \right\} \quad (130)$$

where by assumption the total short-range ion core interaction $V_N^{(s)}$ is a sum of *identical* pair functions, independent of species. If this detailed form of V_N is substituted into the Ψ_N differential equation,

$$\frac{\partial[\Psi_N(\lambda, T)/kT]}{\partial(1/kT)} = V_{N^{(s)}} + \frac{(ze)^2}{D} \left\{ \sum_{j=2}^N \frac{\langle \lambda \xi_j \rangle_T}{r_{1j}} + \sum_{i<j=2}^N \frac{\langle \xi_i \xi_j \rangle_T}{r_{ij}} \right\} \quad (131)$$

The fact has been used here that $V_{N^{(s)}}$ is independent of how anions and cations are distributed on $\mathbf{r}_2 \dots \mathbf{r}_N$.

The temperature-dependent coefficient of each inverse distance term on the right side of equation 131 represents the charge correlation on the corresponding pair of sites under the averaging process $\langle \rangle_T$, defined in equation 129. It is to be expected that a pair of sites separated by a large distance will possess virtually independent charges, so each term will in that case essentially vanish. In addition, these charge correlations also will vanish in the high temperature limit, for then all distributions of charges over $\mathbf{r}_2 \dots \mathbf{r}_N$ are equally likely (random mixing), and no type of pair will predominate. As a result of this latter fact, one deduces that the appropriate boundary condition for integration of differential equation 131 is

$$\lim_{T \rightarrow \infty} \Psi_N(\lambda, T) = V_{N^{(s)}} \quad (132)$$

and so

$$\Psi_N(\lambda, T) = V_{N^{(s)}} + \frac{(ze)^2 kT}{D} \left\{ \sum_{j=2}^N \frac{1}{r_{1j}} \int_0^{1/kT} \langle \lambda \xi_j \rangle_{T'} d \left(\frac{1}{kT'} \right) + \sum_{i<j=2}^N \frac{1}{r_{ij}} \int_0^{1/kT} \langle \xi_i \xi_j \rangle_{T'} d \left(\frac{1}{kT'} \right) \right\} \quad (133)$$

Each charge correlation, $\langle \xi_i \xi_j \rangle_T$ and $\langle \lambda \xi_j \rangle_T$, is in a rigorous sense very complicated, because it depends not only upon the position of the two sites on which the charges being considered reside, but also on where the remaining $N - 2$ sites are placed in the neighborhood of this pair. On the other hand, in dense fluids such as molten salts, a given pair of sites will virtually always be surrounded closely by many other sites which in concert should behave much like the actual fused salt medium. In this sense, we choose to replace the instantaneous effect of the $N - 2$ sites around a given pair, by their time average effect in the liquid. With this approximate interpretation, the averaged products may be taken as those for pairs of sites surrounded by the thermally "smeared" molten salt, and consequently may be evaluated in terms of the molten salt pair correlation functions at temperature T :

$$\begin{aligned}\langle \lambda \xi_j \rangle_T &= \lambda \left[\frac{g_{++}^{(2)}(r_{1j}, \lambda) - g_{+-}^{(2)}(r_{1j}, \lambda)}{g_{++}^{(2)}(r_{1j}, \lambda) + g_{+-}^{(2)}(r_{1j}, \lambda)} \right] \\ \langle \xi_i \xi_j \rangle_T &= \frac{g_{++}^{(2)}(r_{ij}) - g_{+-}^{(2)}(r_{ij})}{g_{++}^{(2)}(r_{ij}) + g_{+-}^{(2)}(r_{ij})}\end{aligned}\quad (134)$$

With these approximations for charge correlations, the pseudo-potential becomes a sum of pairwise additive contributions entirely:

$$\begin{aligned}\Psi_N(\lambda, T) &= V_N^{(s)} + \sum_{j=2}^N \psi(r_{1j}, \lambda) + \sum_{i < j=2}^N \psi(r_{ij}, 1) \\ \psi(r, \lambda) &= - \frac{\lambda (ze)^2 kT}{Dr} \int_0^{1/kT} \tanh \left[\frac{\varphi(r, \lambda, T')}{kT'} \right] d \left(\frac{1}{kT'} \right)\end{aligned}\quad (135)$$

Here the individual pair correlation functions have been eliminated by equation 125 in favor of the more convenient φ . The ψ 's are the temperature-dependent corrections to the actual ion short-range core potential that should be taken into account in computing g_m . In order to make such corrections, φ must be known, and an equation for φ will presently be displayed. This φ equation, however, will be found to contain g_m , so an iterative solution for g_m and φ , to obtain self-consistent values, is in the strict sense a necessity. The advantage of the present formulation however is this: At liquid densities the repulsive ion cores are quite closely packed and (if they may roughly be regarded as properly sized rigid spheres) hence impose stringent geometrical restrictions on possible ion arrangements. Modification of $V_N^{(s)}$ by the ψ 's in equation 135 consequently can cause little re-shuffling of the ion cores (ψ is found to be a predominantly attractive short-range force). g_m therefore is little different from the pair correlation function computed on the basis of $V_N^{(s)}$ alone. If this is the case, the iteration procedure for g_m and φ should converge very rapidly, and in fact a fairly good description of the melt should be obtained without ever correcting the initial approximation to g_m .

The hypothesis that g_m is the pair correlation function in a fluid thermodynamically equivalent to the molten salt can be subjected to experimental test. In particular, it has been found convenient to compare measured isothermal compressibilities with those predicted on the basis of a non-electrolytic fluid of rigid spheres, because this latter may be directly expressed in terms of g_m (66). The anion-

TABLE I

Values of the Anion-Cation Collision Diameter Computed From the Fused Salt Isothermal Compressibilities.

(The corresponding sums of Pauling ionic crystal radii appear in parentheses. All distances are in angstrom units.)

$T, ^\circ\text{C.} =$	600	700	800	900	1000
LiCl (2.41)		2.31	2.26	2.20	2.14
NaCl (2.76)			2.47	2.41	2.34
KCl (3.14)			2.70	2.63	2.55
CsCl (3.50)		3.01	2.93	2.84	2.74
LiBr (2.55)	2.55	2.49	2.43	2.38	2.31
NaBr (2.90)			2.63	2.58	2.51
KBr (3.28)			2.85	2.78	2.70
CsBr (3.64)		3.06	2.98	2.88	2.75
NaI (3.11)		2.88	2.82	2.74	2.66
KI (3.49)		3.09	3.01	2.93	2.82
CdCl ₂ (2.78)	2.50	2.45	2.39		

cation collision diameters estimated for a series of salts in this manner are presented in Table I. The agreement between these computed values and the corresponding sum of Pauling ion radii (realizing that this latter strictly corresponds to solid-state pair potential well minima, rather than the somewhat smaller distances required for strong repulsion) constitutes clear support for our g_m identification.

The functional equation for φ may be derived by essentially the same technique as was used in the lattice theory to obtain a $\bar{\varphi}$ equation (eq. 105) in the preceding section (68). One now starts with the identity:

$$\varphi(r, \lambda) = \frac{kT}{2} \int_0^\lambda d\lambda' \left[\frac{\partial \ln g_{+-}^{(2)}(r, \lambda')}{\partial \lambda'} - \frac{\partial \ln g_{++}^{(2)}(r, \lambda')}{\partial \lambda'} \right] \quad (136)$$

and inserts computed values for the λ' derivatives obtained by differentiation of the definitions (eq. 32) of the respective $g^{(2)}$'s.

Quite analogously to the lattice theory result, the integral equation thus obtained for φ involves triplet correlation functions $g_{\alpha\beta\gamma}^{(3)}$. To have any hope of utilizing the integral equation in determination of φ explicitly, it is necessary to eliminate the $g^{(3)}$'s, and to this end, we elect to invoke the superposition hypothesis (40) whereby each $g^{(3)}$ is replaced by a product of $g^{(2)}$'s:

$$g_{\alpha\beta\gamma}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \cong g_{\alpha\beta}^{(2)}(r_{12})g_{\alpha\gamma}^{(2)}(r_{13})g_{\beta\gamma}^{(2)}(r_{23}) \quad (137)$$

With the aid of this replacement, the integral equation for φ is found to be:*

$$\varphi(r_{12}, \lambda) = \frac{\lambda(ze)^2}{Dr_{12}} - \frac{2\lambda c(ze)^2}{D} \int d^3\mathbf{r}_3 \frac{g(r_{13}, \lambda)}{r_{13}} g_m(r_{23}) \tanh \left[\frac{\varphi(r_{23})}{kT} \right] \quad (138)$$

$$g(r, \lambda) = \frac{1}{\lambda} \int_0^\lambda g_m(r, \lambda') d\lambda', \quad c = N/2\mathcal{V}$$

Once again we shall adhere to the convention that g_m and φ without λ appearing explicitly as argument refer to the fully coupled situation, $\lambda = +1$. If the previous conjecture is valid that g_m is practically equal to the pair correlation function determined by $V_N^{(s)}$ alone, then g_m is λ -independent and identical with g . The position integral in equation 138, replacing the discrete sum in equation 108 of the corresponding lattice theory relation, is over all configurations of a third ion in the vicinity of the chosen pair 1,2 for which φ is being computed; this integral arises strictly from the medium rearrangement which causes the pair potentials of mean force in dense fluids to deviate significantly from the isolated ion pair potential, as remarked in Section IV.

The nature of solutions to nonlinear integral equation 138 may in some measure be determined by a Fourier transform technique. The hyperbolic tangent in the integrand of equation 138 may be linearized if $\varphi(r_{23})$ is sufficiently small. This is the case when r_{23} is large. If we examine for the moment those configurations which also have r_{12} large, then the only positions of ion 3, \mathbf{r}_3 , for which the linearization procedure is invalid, is when 3 is near 2, i.e., r_{13} likewise must be large. But in this event, $g(r_{13}, \lambda)$ differs imperceptibly from its rapidly attained asymptotic value unity. For these configurations, 3 close to 2, then, the integrand will automatically vanish if the Laplacian differential operator with respect to \mathbf{r}_1 is applied to it:

$$\nabla_1^2 \left\{ \frac{g(r_{13}, \lambda)}{r_{13}} g_m(r_{23}) \tanh \left[\frac{\varphi(r_{23})}{kT} \right] \right\} = 0 \quad (r_{13} \text{ large}) \quad (139)$$

Since this vanishing result is not altered by linearization of the hyperbolic tangent, we see that if r_{12} is large and if ∇_1^2 has been

* The reader is referred to reference 68 for details.