Equilibrium Theory of Pure Fused Salts

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CONTENTS

I. Introduction

Inherent in the nature of fused salts are two fundamental complications which the theorist must understand and surmount. In the first place, these substances are representative members of the class of liquids, a state of matter whose microscopic structure and thermodynamic properties have always been difficult to predict quantitatively from the known character of the constituent molecules. In the liquid state, one has appeal neither to the structural regularity of crystalline solids, where atomic motions may be regarded as a superposition of running harmonic waves (normal vibrational modes for the lattice), nor to the situation characteristic of dilute gases, where collisional encounters are rare and occur predominantly between isolated molecular pairs. In common with gases, ordinary liquids have an essentially disordered nature over distances in the substance of macroscopic size. In this article it will become clear, however, that the positions of neighboring particles in liquids, and especially molten salts, are often indicative of a strong local ordering

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influence, or "structure," which is, in the last analysis, a direct result of the qualitative features of the force laws acting between the constituent particles.

The most obvious, and yet striking result of liquid disorder in the large (exempting the case of covalently bound glasses) is the property of fluidity. An adequate understanding of the liquid state must explain this ease of flow, with the seemingly contradictory fact of near-solid packing densities. The flow properties of liquids, vis-à-vis those of the other two states of aggregation, must reflect distinctive modes of molecular motion. These molecular motions in liquids are qualitatively unlike the separate collisions interrupting gas particle linear trajectories (with a well-defined free path length), or the multiply periodic lattice vibrations; they are instead a complicated Brownian motion. The rather small density change occurring upon melting of the solid therefore has a very profound effect on the collective aspects of molecular motion, and we anticipate that the local arrangement of the ions in salts also changes upon melting in a significant fashion to remain consistent with these modes of motion.

The second significant and difficult characteristic of molten salts is, of course, the fact that the constituent particles are electrostatically charged. The extreme range of the Coulomb potential energy, compared, for example, with the Lennard-Jones interaction often quoted for noble gas atom pairs, proved in the early years of theoretical chemistry to provide a classical mystery insofar as understanding the thermodynamic properties of electrolytic solutions was concerned. The resolution proposed in the pioneering work of Debye and Hückel (19) demonstrated lucidly the profound effect that these long-range forces produce. Specifically, the various measurable equilibrium properties of dilute electrolytes in non-electrolytic solvents cannot be expressed as salt concentration power series, as is the case for solutions of non-electrolytes.

Pure molten salts are perhaps the most concentrated electrolytic fluids obtainable by ordinary laboratory techniques. They are most certainly outside the range of applicability of the Debye-Hückel approach. That the extra electrostatic binding in an ionic assembly has primary significance for fused salts is clear from the very high melting and boiling points, as well as the large surface tensions at elevated temperatures measured for these substances. Obviously, the ultimate theoretical analysis of fused salts must explicitly ac-

knowledge the existence of Coulomb interactions, and clarify their role in determining ionic motions and arrangements.

This article is intended to survey some of the existing theoretical approaches to the explanation of the equilibrium properties of pure fused salts. We shall not undertake to investigate the interesting field of transport processes such as electrical and thermal conduction, viscous dissipation, and diffusion, each of which demand establishment of a non-equilibrium state for experimental observation and measurement. However, an elucidation of the equilibrium molecular structure may well serve eventually as a large aid in providing an account of irreversible phenomena close to equilibrium. In addition to covering past work in the field, an effort will be made to point out novel theoretical relations and points of view which seem to merit future detailed examination.

As a preliminary to a review of the powerful Gibbs ensemble technique in equilibrium statistical mechanics, the nature of the forces acting between ions will be discussed at some length. Beside the somewhat trivial exercise of showing how the Coulombic ion–ion interactions arise from the detailed quantum-mechanical theory, it is instructive to analyze the nature of the other types of interactions that occur, and to emphasize the points at which the specifically chemical distinctions between ions of the different elements are important. The natural adjunct to such inquiry is recognition of the existence and nature of complex ions in the melt; unfortunately, limitations on a survey article of this sort prevent any but the most cursory acknowledgment of the fundamentals of modern structural inorganic chemistry, and of their value in predicting the properties of polyatomic species present in melts. On the other hand, it is necessary to stress that the ionic polarizabilities, which may be computed quantum-mechanically, are required for later discussion of the basic dielectric properties of fused salts.

The viewpoint in the following article is that approximate statistical theories of fused salts must be critically evaluated and understood, insofar as it proves feasible, in terms of their relations to and deductions from the rigorous (but often impractically complex) results of fundamental statistical mechanics. In this connection, the intention will be mainly to provide such justifications and criticisms on the basis of informal mathematical and physical intuition. It will soon become apparent to the reader that much remains yet to be

accomplished in this field, especially in the way of carrying out detailed computational programs on the various theoretical analyses available at the time of this writing. The present survey will attempt to indicate not only the lines of past progress, but also the major theoretical stumbling blocks and weaknesses remaining.

II. Forces Between Ions

The most fundamental characteristic of any assembly of molecules or ions, from the standpoint of statistical-mechanical theory, is the type of interactions operative between the constituent particles. To obtain a reasonably detailed account of these interactions and the corresponding forces, it is mandatory to use the notions of quantum mechanics. As a matter of historical fact, one of the early triumphs of wave mechanics in the hands of Heitler and London (32) was satisfactory explanation of chemical covalent binding forces, both qualitatively at first, and later with gratifying numerical agreement with experimental calorimetry and spectroscopy. Likewise, the attractive and repulsive "physical" forces acting between chemically saturated molecules received adequate explanation following London's recognition of the source of dispersion forces (47).

We shall begin this article on fused salts by providing a brief sketch of the quantum-mechanical foundation of intermolecular force theory. Special emphasis will be given to aspects peculiar to ionic particles. The major points to be stressed arise from the qualitative character of the interaction potentials, rather than in their precise numerical computation. It is very often the task of theory in this field to provide a fairly general functional form for intermolecular (interionic in our case) potentials. Subsequently, the remaining adjustable parameters are chosen best to fit some experimental data. A well-known example in this regard is choice of the Lennard-Jones potential depth and breadth parameters to fit measured second virial coefficients or gas viscosities for the noble gases. The main motivation for use of experimental information is the obvious fact that the complete quantum-mechanical theory is impossibly difficult to solve; the traditional sequence of approximation procedures (mentioned below) may be reliable in preserving many important gross features of the interaction potentials, but numerical imprecision is often demonstrably large.
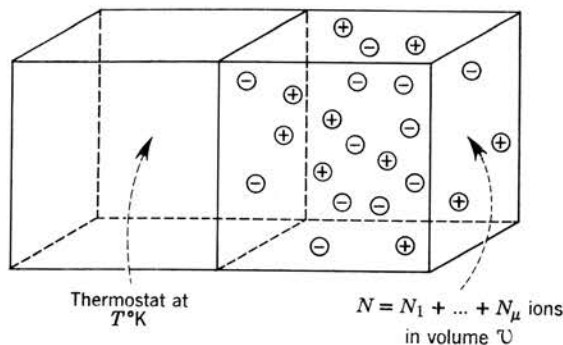
Fig. 1. The thermostated fused salt system in a container with rigid walls.

The molten salt microphysical situation for which we seek a description is a set of ions in a suitable container which, for our purposes, may be thought of as comprising impenetrable walls of a rectangular box (see Fig. 1). Since we ultimately desire to investigate states of thermodynamic equilibrium, it will be necessary to bring this system into thermal contact with a large heat reservoir, or thermostat, characterized by absolute temperature T. It will be presumed that temperature and over-all density are chosen such that the final thermodynamic states of interest are fluid phases, with intensive properties such as local density constant from point to point within each fluid phase. Gravitational effects are significant only insofar as they constrain the denser liquid phase, in a system containing coexistent liquid and vapor, to occupy the bottom of the container.

The individual ions are, of course, composed of orbital electrons surrounding essentially point nuclei. The total electronic and nuclear charges exactly cancel, to leave the entire fused salt system uncharged as a whole.

For a single pure salt whose constituent ions are monatomic, there are just two types of point nuclei which ultimately will form cations and anions. Denote their charges by Z_+e and Z_-e, respectively, with positive integers Z_+ and Z_- the atomic numbers, and e the protonic charge. If there are N_+ and N_- of each of these types of nuclei, then the system must contain precisely $M = N_+Z_+ + N_-Z_-$ electrons.

Except in the case of nuclei with the very lowest atomic numbers, electrons near these nuclei (the inner "core electrons") will be moving

with relativistic velocities. It would be strictly proper, therefore, only to describe the entire nuclear and electronic system by means of a relativistic wave mechanics, i.e., the Dirac four-component matrix equation (63). It is also well known that these rapidly moving electrons, as a result of their relativistic character, are subject to spin-orbit couplings. One recognizes a fortunate circumstance, though, that ordinarily these relativistic effects do not explicitly enter into computation of intermolecular forces. Since they are primarily confined to the inner orbital electrons which are very little affected by the presence of neighboring ions, one may confidently use a completely nonrelativistic quantum theory for intermolecular force calculations. In other words, the absolute error of relativistic origin has virtually no direct effect on intermolecular forces. It would be a mistake to suppose, however, that simultaneously other properties of the ions will be appropriately described, but this fact is of no concern in the present context.

Consequently, we assume that the Schrödinger equation is an adequate formulation of electron and nuclear mechanical motion. The interaction portion, U, of the Hamiltonian operator now consists entirely of the Coulomb potentials for each pair of elementary particles. We split U into a portion strictly involving only nuclear coordinates, U_n, and the remainder, U_e, dependent as well upon positions of the electrons:

$$U = U_n + U_e$$

$$U_n = \sum_{i < j = 1}^{N_+ + N_-} \frac{Z_i Z_j e^2}{|\mathbf{r}_j - \mathbf{r}_i|} \tag{1}$$

$$U_e = \sum_{i < j = 1}^{M} \frac{e^2}{|\mathbf{s}_j - \mathbf{s}_i|} - \sum_{i = 1}^{M} \sum_{j = 1}^{N_+ + N_-} \frac{Z_j e^2}{|\mathbf{r}_j - \mathbf{s}_i|}$$

Position vectors $\mathbf{s}$ refer to electrons, $\mathbf{r}$ to nuclei.

A major simplification in the interatomic force problem results by use of the Born-Oppenheimer separation (11). The nuclei are sufficiently massive by comparison with the electrons that instantaneously their relatively sluggish motions (even at molten salt temperatures) may be disregarded in solving the quantum-mechanical electron problem. Thus the nuclei are regarded as providing a virtually time-independent force field in which the electrons move;

the "fixed" positions $\mathbf{r}_1 \ldots \mathbf{r}_N (N = N_+ + N_-)$ of these nuclei therefore adopt the role of parameters (rather than true quantum-dynamical variables) upon which the eigenfunctions and eigenvalues of the M-body electron problem implicitly depend. The small error in the Schrödinger equation eigenenergies as a result of this separation is known to be of the order of the square root of the electron to nuclear mass ratio (36).

One therefore considers a reduced, or Born-Oppenheimer, wave equation for the M electrons:

$$\mathbf{H}\psi(\mathbf{s}_1 \ldots \mathbf{s}_M) = E\psi(\mathbf{s}_1 \ldots \mathbf{s}_M) \tag{2}$$

$$\mathbf{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{M} \nabla_i^2 + U_e(\mathbf{s}_1 \ldots \mathbf{s}_M)$$

$\hbar$ is Planck's constant divided by 2π, and m_e is the electron mass. Nuclear positions are implicit in both E and U_e. The M electrons, of course, have spin, but in writing the wave function ψ, as in equation 2, the spin coordinates have been suppressed in view of the fact that the Hamiltonian is spin independent. It is to be understood that ψ is normalized and conforms to the Pauli principle; that is, ψ must be antisymmetric with respect to simultaneous interchange of configuration and spin coordinates for any electron pair.

Presuming that it is possible to determine the ground-state energy, E_0, from equation 2 as a function of nuclear coordinates, and since electronic excitations are usually not important for molten salts, the interionic potential energy function, $V_N(\mathbf{r}_1 \ldots \mathbf{r}_N)$, for the molten salt will be taken to be

$$V_N(\mathbf{r}_1 \ldots \mathbf{r}_N) = E_0(\mathbf{r}_1 \ldots \mathbf{r}_N) + U_n(\mathbf{r}_1 \ldots \mathbf{r}_N) - E^\infty \tag{3}$$

The constant E^∞ is the value of E for infinitely separated nuclei, where the quantum state amounts to non-interacting ions. Consequently, V_N vanishes for this separated configuration. The nuclear motion subsequently may in principal be obtained from the *classical* equations of motion for these N particles, with interaction energy V_N. The positions of the various ions in the actual system of interest are then identified at any instant with the coordinates $\mathbf{r}_1 \ldots \mathbf{r}_N$.

With a specific nuclear (ionic) configuration, the M-electron wave function $\psi(\mathbf{s}_1 \ldots \mathbf{s}_M)$ has properties which satisfy a fundamental

theorem of molecular quantum theory. This theorem, which is useful in understanding the nature of forces between the ions of a salt, was discovered independently by Hellmann (33) and Feynman (22). It states simply that the force on each nucleus is precisely the same as would be computed on the basis of classical electrostatics, from a charge density given by the fixed nuclear charges and the local electronic charge density, $\rho_e(\mathbf{r})$. This latter is directly obtained from ψ by integrating $|\psi|^2$:

$$
\begin{aligned}
\rho_e(\mathbf{r}) &= -e \sum_{i=1}^{M} \int d^3\mathbf{s}_1 \ldots d^3\mathbf{s}_M \delta(\mathbf{r} - \mathbf{s}_i) |\psi(\mathbf{s}_1 \ldots \mathbf{s}_M)|^2 \\
&= -eM \int d^3\mathbf{s}_2 \ldots d^3\mathbf{s}_M |\psi(\mathbf{r}\mathbf{s}_2 \ldots \mathbf{s}_M)|^2
\end{aligned}
\tag{4}
$$

where the fact that all electrons must be regarded as indistinguishable has been used. Having computed the forces by this scheme, V_N follows by integration, subject to the vanishing of this latter quantity for infinite separation. Isolated ions of the smaller atomic number elements have spherically symmetric charge distributions in their ground states (closed shells of electron orbitals). If these distributions were preserved separately for each ion, regardless of position, electrostatics then would claim, by way of the Hellmann-Feynman theorem, that V_N would be precisely a sum of Coulombic contributions for the ion-charge pairs if all distances were not so small as to allow ion electron cloud overlaps. Since we shall see this is an oversimplification for V_N, ion charge distortions must be important. A significant value of the Hellmann-Feynman theorem is its recognition that characteristically nonclassical features such as electron spin, and particle indistinguishability (the Pauli principle) have only an indirect effect on intermolecular forces, by the way in which they affect $\rho_e(\mathbf{r})$ through ψ.

Let us first examine the interaction $V_{\gamma\delta}(r)$ between an isolated pair of ions, ion 1 of species γ and ion 2 of species δ, with internuclear separation r. When r is very large, $V_{\gamma\delta}$ vanishes, and in this configuration the electron density around each ion is spherically symmetric. We distinguish two cases: (1) r small enough so significant overlap of electron clouds occurs, and (2) r moderately large to prevent overlap, but still sufficiently small to produce mutual electron cloud polarizations. For the former, r is so small that the set of

orbital electrons for both ions are being forced into the same region of space. The Pauli exclusion principle assures that electrons of the same spin, at least, will avoid one another, so as to displace the electron clouds outward from the region of overlap between nuclei 1 and 2. Furthermore, an attempt to crowd many electrons into a common region (the overlap region) would produce a considerable rise in electron kinetic energy for all electrons involved, regardless of spin. Both effects therefore tend to force electrons out of the region between the nuclei. In this event, the Hellmann-Feynman theorem implies that the nuclei should experience a very powerful repulsion.

Several numerical calculations have been carried out on this repulsive energy for the noble gases (3,62). Since most monatomic ions have completed outer valence shells of electron orbitals (noble gas configurations), it is reasonable to suppose that a qualitatively similar result holds for ion overlap repulsions. It is generally found that this contribution to $V_{\gamma\delta}(r)$ may be represented well by a very rapidly decaying exponential function, with large multiplicative coefficient,

$$V_{\gamma\delta}(r) \rightarrow A \exp(-Br) \qquad (r \text{ small}) \qquad (5)$$

It should be noted that Born and Mayer (10) have been reasonably successful in explaining ionic crystal binding energies, by use of this exponential type of repulsive interaction.

The computional procedures used in obtaining results of type 5 have amounted to first- or second-order quantum-mechanical perturbation theory, where the perturbation is the sum of electron–electron Coulomb repulsions for pairs of electrons, one member of which is included in the electron cloud of ion 1, the other in the cloud of 2. Typically, it is necessary even in the most accurate procedure possible here to utilize properly antisymmetrized product wave functions, built up from only single-electron wave functions of the self-consistent field type, as the set of unperturbed basis functions.

It is the very rapidly rising repulsive portion for $V_{\gamma\delta}(r)$ computed in this way which allows the concept of a meaningful collision diameter for the ion pair 1,2. The typical values of A and B obtained are so large that the fractional change in r causing the value of expression 5 to change from kT to $2kT$ (k is Boltzmann's constant) at molten salt temperatures is very small. In other words, function 5 appears to be almost vertical.

On account of this rapidly rising feature of the repulsive energy
inside the collision diameter, it has often been found advantageous to
replace the exponential decay form by a function qualitatively similar,
but with mathematical properties tending to simplify specific prob-
lems. We mention in this connection two common choices. The
first is the inverse twelfth (or more generally inverse nth) power law,
appearing in the well-known Lennard-Jones potential function.
Secondly, a rigid sphere interaction may be employed as the logical
limit of rapid onset of repulsion.

The only explicit manner in which the nonvanishing ionic charges
are reflected in the parameters of equation 5 is by their effect on the
self-consistent single-electron orbitals used to compute relevant matrix
elements in the perturbation theory. A net positive charge
for cations implies less expanded orbitals than for the cor-
responding isoelectronic noble gas; negative anions have more
expanded orbitals. The resulting change in the collision diameter
for ion pairs can be quite marked. In the case of the analogs—two-
electron hydride ion and helium atom, for example—the crystal
radii are, respectively, 2.08 and 0.93 A. (56).

In the second case of intermediate r, where there is negligible
electron cloud overlap, some important contributions to $V_{\gamma\delta}(r)$ are
rather more subtle. Once again quantum-mechanical perturbation
theory is the tool necessary for detailed calculations. The perturba-
tion now, though, is taken to be the operator H' corresponding to
interaction between the various charge multipoles instantaneously
present at the two ions. Specifically, we choose parallel coordinate
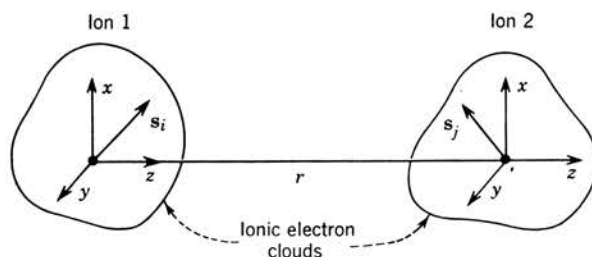systems centered at each nucleus with z axes in the direction $\mathbf{r}$, so

Fig. 2. Coordinate systems used in the multipole interaction perturbation H'.
Electrons in the ionic "clouds" are located by displacement vectors $\mathbf{s}$ giving posi-
tions relative to the respective nuclei.

the x and y axes lie in planes normal to $\mathbf{r}$ through the respective nuclei, as in Figure 2. When the electrons in the respective ionic clouds are specified in position by their components x_i, y_i, and z_i of displacement $\mathbf{s}_i$ from the nucleus to which they are bound, H' may be written as an inverse series in $r = |\mathbf{r}|$:

$$
\begin{aligned}
H' &= \left[\frac{(Z_\gamma - n_\gamma)(Z_\delta - n_\delta)e^2}{r}\right] + \left[\frac{(Z_\gamma - n_\gamma)e^2}{r^2}\sum_{j=1}^{n_\delta} z_j\right. \\
&\left. - \frac{(Z_\delta - n_\delta)e^2}{r^2}\sum_{i=1}^{n_\gamma} z_i\right] + \left[\frac{e^2}{r^3}\sum_{i=1}^{n_\gamma}\sum_{j=1}^{n_\delta}(x_i x_j + y_i y_j - 2z_i z_j)\right] \\
&+ \left[\frac{(Z_\gamma - n_\gamma)e^2}{r^3}\sum_{j=1}^{n_\delta}(z_j^2 - {}^1\!/_2 x_j^2 - {}^1\!/_2 y_j^2)\right. \\
&\left. + \frac{(Z_\delta - n_\delta)e^2}{r^3}\sum_{i=1}^{n_\gamma}(z_i^2 - {}^1\!/_2 x_i^2 - {}^1\!/_2 y_i^2)\right] + 0(r^{-4}) \\
&= H'_{cc} + H'_{cd} + H'_{dd} + H'_{cq} + 0(r^{-4})
\end{aligned}
\tag{6}
$$

Summation index i has here been used only for the n_γ electrons of the ion 1, and j only for the n_δ electrons of ion 2.

The various terms in H' may easily be recognized. The leading contribution, H'_{cc}, dropping off with inverse distance, is the Coulomb interaction operator between the two ions regarded as point charges. H'_{cd}, decreasing with distance by an extra r^{-1} factor, represents the instantaneous electrostatic interaction of charge on one ion with the dipole moment of the other, as well as the reverse; the interaction again is that for point multipoles. Likewise, H'_{dd}, varying as r^{-3}, is a dipole–dipole term. The last explicitly indicated contribution is for the interaction of a point charge–point quadrupole variety, and is also an r^{-3} perturbation. The neglected terms, $0(r^{-4})$, amount to charge–octupole, dipole–quadrupole, etc. interactions. When r is not too small (greater than four or five ionic collision diameters), the multipole expansion converges sufficiently rapidly that neglect of these higher order terms is appropriate.

The unperturbed wave function for the $n_\gamma + n_\delta$ electrons may be taken as simply a product of the individual isolated ion wave functions; since overlap is assumed negligible, it is unnecessary to anti-symmetrize the resulting product with respect to interionic electron permutations, in computing the necessary matrix elements. For ions of small atomic number, the isolated ion wave functions are spheri-

cally symmetric and are Russell-Saunders $^1S_0$ states, so only a single such joint wave function is appropriate. For individual ions with more complicated electronic structure, several potential energy curves eventually would be computed relating to the various joint wave functions for the two ions that may be constructed (corresponding, for example, to different values of total electronic spin and angular momentum along the internuclear axis). In these cases, it would be necessary to seek some average potential curve according to a Boltzmann factor weighting for the temperature of interest.

In the first order of perturbation, where the computed energy is symbolized as usual by the diagonal matrix element notation $\langle 0|H'|0\rangle$ (0 standing for the unperturbed ground state), only H'_{cc} yields a nonvanishing result: as expected this is the ion–ion Coulomb potential. The diagonal matrix elements of the other members of H' vanish for these spherically symmetric states. It is in second order, though, that nontrivial results are obtained; the nondiagonal matrix elements which occur appear squared:

$$\sum_{k \neq 0} \frac{\langle 0|H'|k\rangle\langle k|H'|0\rangle}{\epsilon_k - \epsilon_0}$$

Here, the ϵ's are the unperturbed energies and summation includes all excited intermediate states k for the two-ion system. The energies of interaction corresponding to each of $H'_{cc}...H'_{cq}$ in this second order have the following r dependence:

H'_{cc}: Vanishes in second (and each higher) order
H'_{cd}: r^{-4}
H'_{dd}: r^{-6}
H'_{cq}: r^{-6}

The physical meaning of the H'_{cd} perturbation is that of dipole polarization of the electron cloud of one ion due to the electric field surrounding the charge of its neighboring ion. In fact, the r^{-4} dependence is precisely that expected for a charge and an induced dipole. It is therefore proper to call this type of force an *induction* force. In cases of interest, it may be evaluated either by complete quantum-mechanical calculation, or by use of experimentally measured ion polarizabilities α_γ and α_δ (from refractive index measurements), and the instantaneous electric field at the position of that ion.

The H'_{dd} contribution is usually called the London dispersion force. Physically, it amounts to the fact that orientations of instantaneous dipole moments of the two electron clouds are correlated. They prefer to adopt simultaneously antiparallel directions to lower the total interaction energy. Consequently, this force is always attractive. Dispersion forces have been computed for noble gases (57) with results that are in reasonably good accord (when combined with the repulsive core calculations) with dilute gas equation of state and viscosity measurements. The second-order perturbation method, then, is apparently reliable for this contribution. No computations, however, have been carried out for ions. On a qualitative basis, though, the tighter average binding of electrons in cations relative to the isoelectronic noble gas implies less ease of spontaneous dipole formation. Consequently, the numerical multiplicative coefficient of r^{-6} in the dispersion interaction for a pair involving cations is depressed below the noble gas value. Naturally, the reverse is true in the case of anions. In any event, the largest share of the dispersion force will be due to the least tightly bound outer shell of electrons. With a pair of ions with noble gas atom structures for their ground states, the largest contribution to the dispersion energy in second-order perturbation theory will involve both ions in the intermediate state (k) with electrons excited to the lowest lying p orbitals.

London (47) has proposed a simple means of estimating the numerical coefficient for the dispersion force. If the polarizabilities of ions 1 and 2 are denoted, respectively, by α_γ and α_δ, and the energy required for removal of an electron from each by I_γ and I_δ, the London approximation has the simple form:

$$V_{\gamma\delta}^{\text{disp}}(r) \cong - \frac{3\alpha_\gamma\alpha_\delta I_\gamma I_\delta}{2(I_\gamma + I_\delta)r^6} \qquad (7)$$

Although originally proposed for neutral atoms or molecules, it should apply as well to our ionic case. In a recent review article, Pitzer (57) has discussed in detail the derivation of equation 7, along with related formulas for $V_{\gamma\delta}^{\text{disp}}(r)$ attributed to Slater and Kirkwood (65) and Kirkwood and Müller (53).

The final contribution to $V_{\gamma\delta}(r)$, arising out of H'_{cq}, is likewise an r^{-6} attractive interaction. It amounts to induction of a static
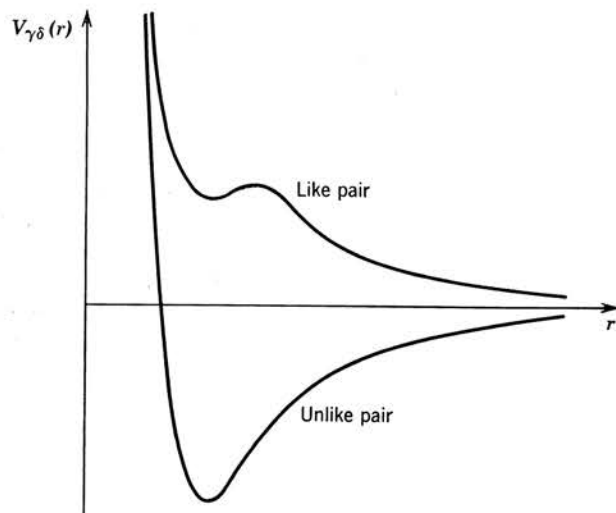
Fig. 3. Isolated ion pair interaction curves.

quadrupole moment in one ion by the *gradient* of electric field at its center, due to the other ion's net charge. Obviously, no such force can exist between uncharged noble gas atoms, so this additional force, usually not recognized, is peculiar to the ionic case.   In this second-order perturbation scheme at least, it will mainly be due to the lowest lying states with excited d electrons, which have the proper quadrupole symmetry.   Since the energy level scheme for light atoms generally places these d orbitals higher than the p orbitals required for the dispersion attraction, it is probably true that the major contribution to the total inverse sixth power attractive energy between ions is just the London dispersion portion.   The charge–quadrupole contribution may also properly be termed an induction force.

The total ion pair potential $V_{\gamma\delta}(r)$ may now be written:

$$V_{\gamma\delta}(r) = A_{\gamma\delta}e^{-B_{\gamma\delta}r} - \frac{C_{\gamma\delta}}{r^6} - \frac{[(z_\gamma e)^2\alpha_\delta + (z_\delta e)^2\alpha_\gamma]}{2r^4} + \frac{z_\gamma z_\delta e^2}{r}$$

$$z_\gamma = Z_\gamma - n_\gamma; \quad z_\delta = Z_\delta - n_\delta; \quad A_{\gamma\delta}, B_{\gamma\delta}, C_{\gamma\delta} > 0 \qquad (8)$$

Figure 3 indicates roughly the qualitative nature of $V_{\gamma\delta}(r)$ for a pair of ions with like and with unlike charge signs. The existence or non-existence of a minimum for the like pair is contingent on the

relative values of charge, dipole and quadrupole polarizability, dispersion attraction, and ion core size (collision diameter).

The actual molten salt consists of $\frac{1}{2}N(N-1)$ distinct ion pairs within the container. To obtain the total interaction energy V_N for a given set of ion positions $\mathbf{r}_1 \ldots \mathbf{r}_N$, it is necessary to specify an approximate rule for conversion of the isolated ion pair result, to this many-ion case. The inverse distance ion-charge Coulomb interactions $z_\gamma z_\delta e^2/r$, will always be additive, as a general quantum-mechanical result following definition of the H'_{cc} perturbations. It is necessary to suppose in addition that the repulsive ion core, and the attractive dispersion forces are likewise additive. The deviations from this ideal situation (at least for the dispersion forces) have been investigated theoretically, and are discussed in a review by Kihara (39). The errors involved are not large, and it is convenient to disregard them in the interests of simplicity. However, it is entirely inappropriate to suppose that the r^{-4} dipole induction contribution, in equation 8, is additive. The total induced dipole for any given ion may be regarded as a vector sum of dipoles due to all electric field sources surrounding this polarized ion. But the local electric field at the ion is a result not only of the entire set of ionic charges, but the other induced dipoles as well, which themselves depend upon the entire set of ionic charges and dipoles. In other words, the induced dipole potential energy is in the strict sense unavoidably a many-body interaction in the liquid salt system of interest.

We shall tentatively suppose that the charge-induced quadrupole r^{-6} energies are on the average also additive, so they may be combined with the dispersion energies in V_N. The result then is a joint inverse sixth power attractive interaction for each ion pair, whose numerical coefficient combines these two types of perturbation.

To find V_N, therefore, one adds up the ion core repulsions, r^{-6} attractions, and the r^{-1} Coulomb interactions for all pairs. With this subsequently must be combined the additional (negative) induced dipole energy. This latter is obtained as solution of the classical electrostatic problem of a set of point charges, and polarizable point particles, at $\mathbf{r}_1 \ldots \mathbf{r}_N$.

There still remains the problem of choosing the constants $A_{\gamma\delta}$, $B_{\gamma\delta}$, and $C_{\gamma\delta}$ in equation 8. Low-temperature data on the solid phase for the salt of interest are especially useful in this connection.

For salts which crystallize in lattices sufficiently symmetrical that each ion is a center of symmetry, the electric field at each nucleus vanishes, so no static polarization interactions occur. The lattice near-neighbor distance may be used to fix the unlike ion pair potential minimum, and the sublimation energy its depth. Furthermore, the compressibility should determine the curvature at this minimum. The remaining undetermined constants may be chosen so as to conform to London's rule, equation 7, and the known crystallographic radii of the ions.

To this point, our discussion of forces has consistently supposed that ions refrained from covalent chemical binding. However, there is virtually a continuous spectrum of substances ranging from those whose melts are almost exclusively ionic (NaF), to salts where the species present are primarily covalently bound complex ions or molecules (such as the mercuric halides). At the two extremes, the relevant species present are easily distinguishable and may with virtually no ambiguity be regarded as the fundamental "building blocks" of which the melt is composed. Thus, in fused KNO_3, the two significant species are clearly potassium cation and the stable polyatomic nitrate anion.

Not only are a variety of experimental techniques available for distinguishing what bound species are present (simple molecules or complex ions), but often their concentrations may readily be estimated. To be precise in a statistical-mechanical theory of melts containing these clear-cut polyatomic species, it would be necessary to include for each such particle a set of internal coordinates describing rotational and vibrational degrees of freedom; in principle, the fundamental statistical methods to be described in later sections are capable of dealing with these additional complications, though often with considerable extra labor. In some cases, it will be possible to take advantage of rapid rotations to provide a sphericalization of these polyatomic species. Furthermore, it is often sufficient to consider center-of-mass translational degrees of freedom for the entire set of particles to be uncoupled from vibrations and rotations.

The interparticle potential energy, V_N, for an assembly of N polyatomic particles could be built up of contributions arising from each atom of the complex particles, using the pair potential energy form, equation 8, already adduced in this section, with parameters appropriate to bound atoms. Under the condition of rapid rotation

of the polyatomic species, the resulting rotation-averaged V_N would have the same character as for monatomic particles (pairwise additive, except for the induced dipole contribution), and is amenable to ready use in computing the microscopic structure of the liquid.

The greatest conceptual difficulty, so far as the statistical mechanics of liquids is concerned, occurs in the fairly extensive class of borderline melts, where liquids are only partially and indistinctly associated, or where large polymeric complexes appear to be present. Typical examples are BeF_2 (48) and $ZnCl_2$ (49). The trouble is, on the one hand, that most neighboring pairs of particles are not sufficiently strongly associated to present a clear and unambiguous case of stable chemical (as distinguished from electrostatic) binding. But on the other hand, the additional forces which are covalent (or "chemical" in nature are sufficiently strong to modify the thermodynamic functions as well as local structure to a significant degree. If these chemical forces were central and pairwise additive, as are (approximately) the nonpolarization "physical" forces treated earlier, they would present no problem. But they are not this simple; chemical bonds are obviously directional, and they are saturating, since a given atom can bond to only certain numbers of neighbors, in accord with the usual chemical properties for the element in question.

It will eventually be necessary to include what is known about the qualitative features of chemical bonding forces within the framework of existing practical methods of statistical mechanics which explicitly utilize intermolecular force expressions. At present, however, such techniques are conspicuously lacking in liquid state theory. In the following, therefore, when it becomes necessary to use the potential energy function V_N for the N salt ions, it will be supposed that these particles are suitably stable chemical entities, so V_N itself contains no chemical binding, or valence, interactions.

III. Local Dielectric Properties

Section II has reviewed the fundamental bases for our qualitative understanding of the various types of forces acting between the ions in a molten electrolyte. The forces could be classified roughly by the number of particles simultaneously involved. The Coulomb r^{-1} interaction as well as the London r^{-6}, and repulsive core potentials act only between pairs, and are thus (at least in good approximation

for the latter two) pairwise additive; this simple feature is helpful in visualizing these components of V_N for given $\mathbf{r}_1 \ldots \mathbf{r}_N$. The nature of polarization forces, though, is entirely different. An ion's charge will thus induce simultaneous dipoles in neighboring ions, which then will interact not only among themselves, but will likewise induce instantaneous dipoles in yet other ions. Since the induced dipole–induced dipole interactions fall off with distance sufficiently slowly (r^{-3} in a given direction relative to one such dipole), the entire molten salt is simultaneously involved in producing these polarization energies, rather than just sets of a small finite number of ions independent of the system size.

It is the purpose of this section, however, to demonstrate explicitly the manner in which the usual dielectric constant hedge against the complicated nature of the truly many-body polarization forces may be systematically accomplished. The fact that our results indicate the validity of the usual use of a dielectric constant for the fused salt medium is in itself hardly startling, and has always been anticipated for liquid electrolytes by physical intuition. The value of a careful approach, though, lies first in the derivation of explicit formulas for local (i.e., molecular) dielectric properties, and secondly, in clear recognition of what is being neglected in replacement of the many-body polarization effects by one- and two-body dielectric continuum interaction energies.

For simplicity, it will be assumed in this analysis that the molten salt is in a single homogeneous fluid phase. The total interaction for the N ions, $V_N(\mathbf{r}_1 \ldots \mathbf{r}_N)$, may be separated for the present purposes into an electrostatic part, $V_N^{(e)}(\mathbf{r}_1 \ldots \mathbf{r}_N)$, including both the Coulomb charge–charge potentials as well as effects arising from induced dipoles; and the remaining $V_N^{(s)}(\mathbf{r}_1 \ldots \mathbf{r}_N)$ which collects all the short-range interactions (dispersion, core-repulsion), and which is independent of the ion charges. $V_N^{(s)}$, it has already been remarked, may be considered pairwise additive. To each ion $1 \leq i \leq N$ we have assigned a polarizability α_i. The static charges $z_i e$ and induced dipoles will set up an instantaneous electrostatic potential in the system $\psi(\mathbf{r})$. Implicit in this function ψ must be all N ion positions $\mathbf{r}_1 \ldots \mathbf{r}_N$.

The momentary dipole $\mathbf{u}_i$ induced in ion i is equal to α_i times the electric field at the center of i due to all other charged and polarized ions in the system. This electric field is equal to the negative

gradient at $\mathbf{r}_1$ of $\psi_i(\mathbf{r})$, where this latter quantity is ψ with the self-potential of ion i removed:

$$\psi_i(\mathbf{r}) = \psi(\mathbf{r}) - \frac{z_i e}{|\mathbf{r} - \mathbf{r}_i|} - \frac{\mathbf{u}_i \cdot (\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^3} \tag{9}$$

Thus,

$$\mathbf{u}_i = -\alpha_i \nabla \psi_i(\mathbf{r}_i) \tag{10}$$

The electrostatic potential $\psi(\mathbf{r})$ has just the familiar form

$$\psi(\mathbf{r}) = \sum_{j=1}^{N} \left\{ \frac{z_j e}{|\mathbf{r} - \mathbf{r}_j|} + \frac{\mathbf{u}_j \cdot (\mathbf{r} - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}_j|^3} \right\} \tag{11}$$

appropriate to a set of point charges $z_j e$ and dipoles $\mathbf{u}_j$. Using equation 10, of course

$$\psi(\mathbf{r}) = \sum_{j=1}^{N} \left\{ \frac{z_j e}{|\mathbf{r} - \mathbf{r}_j|} - \alpha_j \frac{\nabla \psi_j(r_j) \cdot (\mathbf{r} - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}_j|^3} \right\} \tag{12}$$

An elementary theorem of electrostatics (69) provides the electrostatic interaction energy $V_N{}^{(e)}$, as one-half the sum over the region spanned by our salt system of the product of the point charges times the self-energy-corrected potentials for those points. As a result, equations 9 and 12 lead trivially to

$$V_N{}^{(e)}(\mathbf{r}_1 \ldots \mathbf{r}_N) = \sum_{i<j=1}^{N} \frac{z_i z_j e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$- \frac{1}{2} \sum_{i=1}^{N} \left[\sum_{\substack{j=1 \\ \neq i}}^{N} z_i e \alpha_j \frac{\nabla \psi_j(\mathbf{r}_j) \cdot (\mathbf{r}_i - \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^3} \right] \tag{13}$$

The doubly summed second portion of expression 13 represents the many-body polarization interactions. Their troublesome nature arises from the implicit dependence of ψ_j on all ion positions.

The square-bracketed single sum in equation 13 is the interaction energy of the ion i with all of the instantaneously induced dipole moments of the other $N - 1$ ions. Most of these latter are located at large distances from i on the molecular scale, and their dipoles appear from $\mathbf{r}_i$ to be oriented nearly at random (i.e., independent of the position $\mathbf{r}_i$). Therefore their individual contributions to the bracket largely cancel one another. This amounts to recognizing

that only small fluctuations are to be observed about the continuum behavior for this large assembly of dipoles. The most important fluctuations are those occurring close to the ion of interest at $\mathbf{r}_i$, both because the number of near neighbors is small (so that statistical laws of large numbers are less effective in "homogenizing" this nearby region), and because the relevant charge–dipole interaction is large at these small separations.

In accord with these ideas, we make use of an expansion procedure for a function $f(\mathbf{r}_i)$ of the position of ion i, which also depends implicitly on the entire residual set of $N - 1$ positions $\mathbf{r}_1 \ldots \mathbf{r}_{i-1}$, $\mathbf{r}_{i+1} \ldots \mathbf{r}_N$. Symbolically,

$$
f(\mathbf{r}_i) \equiv \langle f \rangle^{(i)} + \sum_{\substack{j=1 \\ \neq i}}^{N} [\langle f \rangle^{(ij)} - \langle f \rangle^{(i)}]
$$

$$
+ \sum_{\substack{j<k=1 \\ \neq i}}^{N} [\langle f \rangle^{(ijk)} - \langle f \rangle^{(ij)} - \langle f \rangle^{(ik)} + \langle f \rangle^{(i)}]
$$

$$
+ \sum_{\substack{j<k<l=1 \\ \neq i}}^{N} [\ldots] + \ldots \tag{14}
$$

The angular brackets $\langle\ \rangle^{(i\,\cdots\,s)}$ denote averages over the entire set of accessible configurations and momenta ($\mathbf{p}$) for the system, but with the n ions $i \ldots s$ held fixed at $\mathbf{r}_i \ldots \mathbf{r}_s$:

$$
\langle f \rangle^{(i\,\cdots\,s)} = \frac{\int f P^{(N)}(\mathbf{r}_1' \ldots \mathbf{p}_N')\delta(\mathbf{r}_i - \mathbf{r}_i') \ldots \delta(\mathbf{r}_s - \mathbf{r}_s')d\mathbf{r}_1' \ldots d\mathbf{p}_N}{\int P^{(N)}(\mathbf{r}_1' \ldots \mathbf{p}_N')\delta(\mathbf{r}_i - \mathbf{r}_i') \ldots \delta(\mathbf{r}_s - \mathbf{r}_s')d\mathbf{r}_1' \ldots d\mathbf{p}_N} \tag{15}
$$

The phase space probability density, or weighting function, $P^{(N)}$, appearing in the average value definitions (eq. 15) will later be identified as the Gibbsian canonical ensemble distribution.

The successive terms in equation 14 have a fairly straightforward interpretation. The leading quantity, $\langle f \rangle^{(i)}$, represents the average value of f over all positions (and momenta) of the remaining $N - 1$ ions. It is this replacement of the instantaneously position-fixed set of polarizable ions surrounding i by their time (or ensemble) average behavior that is equivalent to regarding ion i as being alone in a dielectric continuum. The succeeding terms on the right-hand side of equation 14, however, act to correct the error in this entirely homogeneous approximation for the surroundings of i. The quantity

$[\langle f \rangle^{(ij)} - \langle f \rangle^{(i)}]$ appearing next in equation 14 is the instantaneous extra effect on f of an ion j (which is not "smeared out" as in $\langle f \rangle^{(i)}$) and, as shown, such correction must be made for all $N - 1$ ions not equal to i. But in computing each of these corrections, the residual set of $N - 2$ ions ($\neq i,j$) are regarded as "smeared" into a dielectric continuum surrounding the pair i,j. In like fashion, the third set of terms in equation 14 takes into account the fact that actually there were discrete ion pairs j,k in the vicinity of i; etc. In principle it is necessary to go to N such terms to make the identity, equation 14, rigorously exact, but for certain choices of f we might reasonably expect this fluctuation expansion to converge rapidly.

This will in fact be precisely our point of view concerning the square bracket in equation 13, which is now the specific choice for f. We truncate the resulting expansion, equation 14, after the second (single-particle fluctuation) class of terms, to obtain

$$
\left[\sum_{\substack{j=1 \\ \neq i}}^{N} z_i e \alpha_j \frac{\nabla \psi_j(\mathbf{r}_j) \cdot (\mathbf{r}_i - \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^3} \right] \cong z_i e \left\langle \sum_{\substack{j=1 \\ \neq i}}^{N} \alpha_j \frac{(\mathbf{r}_i - \mathbf{r}_j) \cdot \nabla \psi_j(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^3} \right\rangle^{(i)}
$$

$$
+ z_i e \sum_{\substack{j=1 \\ \neq i}}^{N} \left[\left\langle \sum_{\substack{k=1 \\ \neq i,j}}^{N} \alpha_k \frac{(\mathbf{r}_i - \mathbf{r}_k) \cdot \nabla \psi_k(\mathbf{r}_k)}{|\mathbf{r}_i - \mathbf{r}_k|^3} \right\rangle^{(ij)} \right.
$$

$$
\left. - \left\langle \sum_{\substack{k=1 \\ \neq i}}^{N} \frac{(\mathbf{r}_i - \mathbf{r}_k) \cdot \nabla \psi_k(\mathbf{r}_k)}{|\mathbf{r}_i - \mathbf{r}_k|^3} \right\rangle^{(i)} \right] \quad (16)
$$

Upon inserting this result into expression 13 for $V_N^{(e)}$, the various terms are readily identifiable. Of course, the same point charge–point charge Coulomb potentials occur again unaffected by the averaging procedure (they are the first sum in 13). The leading contribution from the inserted fluctuation expansion represents the interaction of each ion i with the average polarization field surrounding it; this polarization field is spherically symmetric for a monatomic ion and its ambient medium. The corresponding contribution to $V_N^{(e)}$ is the so-called Born cavity energy.

If the average surroundings of ion i are characterized as a linear dielectric continuum with radially varying dielectric constant $D_\gamma(r)$ as shown in Figure 4 (ion i is species γ), then the average polarization density $\mathbf{P}_\gamma$ is radially directed and likewise symmetric, and is given by

$$
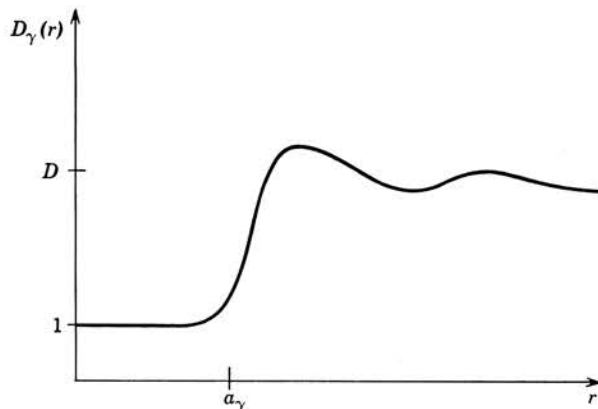4\pi \mathbf{P}_\gamma(\mathbf{r}) = [D_\gamma(r) - 1] \mathbf{E}_\gamma(\mathbf{r}) \quad (17)
$$

Fig. 4. Qualitative nature of the local dielectric "constant," $D_\gamma(r)$, surrounding a central ion of type γ located at the origin. The radial distance a_γ roughly corresponds to the distance of closest approach to this ion.

where $\mathbf{E}_\gamma$ is the average local electric field at distance r from ion i,

$$\mathbf{E}_\gamma(\mathbf{r}) = -\frac{z_\gamma e \mathbf{r}}{D_\gamma(r) r^3} \tag{18}$$

The Born cavity energy is therefore found by integration over all space of the interaction of the dipole density $\mathbf{P}_\gamma$ with the charge on ion i producing it:

$$
\begin{aligned}
U_{bc}^{(i)} &= \int d^3\mathbf{r} \left(\frac{z_\gamma e}{2}\right) \frac{\mathbf{P}_\gamma(\mathbf{r}) \cdot \mathbf{r}}{r^3} \\
&= -\frac{(z_\gamma e)^2}{2} \int_0^\infty \frac{dr}{r^2} \left[1 - \frac{1}{D_\gamma(r)}\right]
\end{aligned}
\tag{19}
$$

The local dielectric constants $D_\gamma(r)$ for all types of ions have the two general properties:

(a) $\lim\limits_{r \to 0} D_\gamma(r) = 1$, since no ions can penetrate the central ion's repulsive core, so that the dielectric constant exhibits the free-space value.

(b) $\lim\limits_{r \to \infty} D_\gamma(r) = D$, the macroscopic dielectric constant. It is presumed that this latter is adequately approximated, in practical cases, by the square of the fused salt refractive index at optical
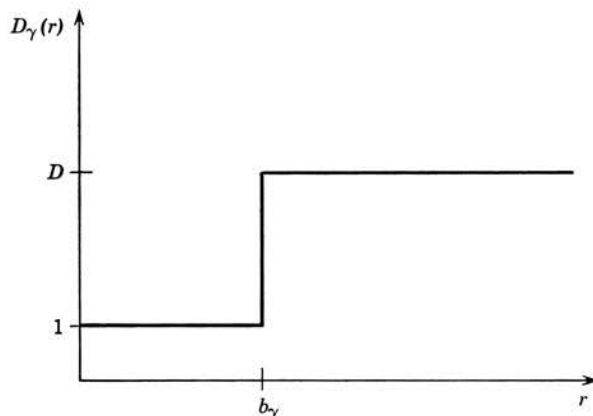
Fig. 5. The idealized local dielectric constant radial variation corresponding to a sharply defined spherical cavity in an otherwise uniform dielectric continuum.

frequencies (this is typically around 2–5).* The simplest local dielectric picture which might reasonably be adopted consistent with the general properties (a) and (b) is that of a sharply delineated spherical cavity of radius b_γ in the dielectric continuum, outside of which the dielectric constant is everywhere D, the macroscopic value. This model is indicated in Figure 5. In this simplified case equation 19 may immediately be integrated to yield

$$U_{bc}{}^{(i)} = - \frac{(z_\gamma e)^2}{2b_\gamma} \left(1 - \frac{1}{D} \right) \tag{20}$$

Since $D(r) \geq 1$, the Born cavity energy is never positive, as may be seen either from the general expression (eq. 19), or more simply from equation 20. Due to the fact that the Born cavity energies are position independent within homogeneous fluid phases, they simply shift downward the total N-ion interaction energy, V_N, and can have no direct effect on the way in which ions are arranged in the bulk of the molten salt.

* Implicit here is the assumption that no electronic transitions for the ions lie close in energy to that of the measuring optical radiation. This will certainly be true for the simple alkali halides, and it is probably valid for other uncolored melts. It is in principle possible to separate the anomalous optical dispersion due to low-lying electronic transitions near the optical region in other cases, if the frequencies and oscillator strengths of the transitions are known.

The remaining fluctuation terms arising from the previous substitution of equation 16 in equation 13 can be given a similar, though somewhat more complicated interpretation. The effect of performing the indicated average value operations is to recognize that the term depending explicitly on the position of pair i,j (with superscript indices occurring in that order for these two ions) represents the interaction energy of the charge $z_\gamma e$ on ion i (still in its dielectric cavity as before) with (1) the dipole moment induced by i in ion j; and (2) the *excess* polarization density in the dielectric medium surrounding fixed i and j, beyond what would be present if just ion i were constrained to be fixed in position. One must realize that in the entire expression 13 there will arise two fluctuation quantities corresponding to i and j fixed. The other term's physical significance is also given by (1) and (2), but with the roles of i and j reversed. It is convenient to combine these two terms.

When ions i (species γ) and j (species δ) are constrained to be a distance r apart, which is comparable to ordinary molecular dimensions, it would generally be necessary to concede that the dielectric cavities surrounding the two ions are no longer spherically symmetric. Of course they become almost precisely so as r increases beyond, let us say, ten or more ionic diameters. Nevertheless, it is certainly informative, and probably not far from the quantitative state of affairs, to suppose that at all distances r the previous sharply defined spherical Born cavities (radii b_γ and b_δ) exist in the uniform continuum of dielectric constant D. With this double Born cavity picture in mind, it is in principle possible to compute the relevant contribution to $V_N^{(e)}$ for the pair i,j,* the result for which we quote when $r \gg b_\gamma + b_\delta$ (so that virtually uniform electric fields act on each cavity), combined with the i,j Coulomb term from the leading sum in equation 13:

$$V_{\gamma\delta}{}^{(e)}(r) = \frac{z_\gamma z_\delta e^2}{Dr} + \frac{(D-1)b_\delta{}^3 - (D+2)\alpha_\delta}{(2D+1)b_\delta{}^3 - 2(D-1)\alpha_\delta} \cdot \frac{(z_\gamma e)^2 b_\delta{}^3}{2Dr^4}$$

$$+ \frac{(D-1)b_\gamma{}^3 - (D+2)\alpha_\gamma}{(2D+1)b_\gamma{}^3 - 2(D-1)\alpha_\gamma} \cdot \frac{(z_\delta e)^2 b_\gamma{}^3}{2Dr^4} \quad (21)$$

* If $r < b_\gamma + b_\delta$, the two spherical cavities join to form a singly connected bispherical region. The electrostatic problem to be solved in this geometry is unfortunately much more difficult than when the two cavities are distinct, and $r > b_\gamma + b_\delta$.

For large r, at any rate, $V_{\gamma\delta}{}^{(e)}(r)$ as shown is the proper form of the entire ion pair contribution to the electrostatic interaction energy. The last two terms in equation 21 are the interaction of charges $z_\gamma e$ and $z_\delta e$, respectively, with the total dipole moment induced in the other ion and its cavity. For smaller r, terms in larger negative powers of r will appear in $V_{\gamma\delta}{}^{(e)}(r)$, though their explicit computation becomes difficult even for the idealized spherical cavities. Kirkwood (41) has considered the effect of interactions of type 21 on the thermodynamic properties of electrolytic solutions, but apparently no explicit use has been made of this effective potential function in molten salt considerations.

An empty cavity amounts to setting the charge and polarizability of its contained ion equal to zero, and for such case, equation 21 demonstrates that a cavity alone is always repelled from an electrostatic charge. In a similar fashion, setting the cavity radius to zero, it is seen that an isolated polarizable point is always attracted to a charge. Accordingly, these two effects, in the case at hand, tend to cancel one another to give an interaction dropping off as r^{-4}, which is less in magnitude in liquids than *in vacuo*. These r^{-4} terms shown explicitly in equation 21, as well as the terms occurring at smaller r, are probably not too large in liquids for most distances of separation. In the lack of strong evidence to the contrary, it is probably sufficient to retain only the leading term in 21 for the electrostatic potential in computing molten salt properties. Our later considerations will be sufficiently general, though, that these dielectric cavity and polarizability terms may formally be included as part of the short-range pairwise additive interactions between ions, $V_{\gamma\delta}{}^{(s)}(r)$.

We remark that these spherical cavity considerations may be employed to provide an elementary dielectric constant expression for the molten salt by a method due to Onsager (55). One finds the implicit relation

$$\frac{D-1}{12\pi D} = \sum_{\gamma=1}^{\mu} \frac{\rho_\gamma \alpha_\gamma b_\gamma{}^3}{(2D+1)b_\gamma{}^3 - 2(D-1)\alpha_\gamma} \qquad (22)$$

for a salt containing μ different types of ions, respectively present in the concentrations ρ_γ. We shall have later reference to the total particle density variation of D; since equation 22 may be solved for D, it provides a convenient means for determining such variations. A more precise computation of local dielectric constants $D_\gamma(r)$, as well

as their asymptotic value D, would have to follow the procedure outlined for nonpolar liquids by Brown (13), when suitably generalized to mixtures, and to the region surrounding a fixed set of ions.

In conclusion, therefore, we have been able to replace the electrostatic part of the actual V_N, containing the many-body polarization interactions, by a sum of single-ion $[U_{bc}{}^{(i)}]$ and ion-pair $[V_{\gamma\delta}{}^{(e)}(r)]$ interactions. Since for non-associated salts, the non-electrostatic forces as well may be taken as pairwise additive, the effective form for V_N that may be used is now especially convenient:

$$V_N(\mathbf{r}_1 \ldots \mathbf{r}_N) = \sum_{i=1}^{N} U_{bc}{}^{(i)} + \sum_{i<j=1}^{N} [V_{\gamma\delta}{}^{(s)}(r) + V_{\gamma\delta}{}^{(e)}(r)] \quad (23)$$

$$\gamma = \gamma(i); \quad \delta = \delta(j)$$

Henceforth, we shall suppose that this reduction has been made when, in discussing the methods of evaluating molten salt thermodynamic properties and microscopic structures, it is necessary to refer to an explicit potential-energy function.

IV. Fundamentals in the Statistical Theory

The preceding section has been devoted to methods of finding an appropriate interaction potential for an assembly of ions, which is not unmanageably complicated. It is, after all, this interaction energy which determines the observed macroscopic properties of a molten salt. Having obtained a proper $V_N(\mathbf{r}_1 \ldots \mathbf{r}_N)$, it is subsequently the task of statistical mechanics to provide a deductive procedure for computing the fused salt properties of interest. As indicated in the introductory remarks, we shall attack only the problems of predicting equilibrium properties; in other words, the fused salt system will have no gradients of temperature, composition, or pressure (gravitational effects are entirely inconsequential for homogeneous systems of modest dimensions).

Figure 1 showed in schematic fashion a container of volume $\mathcal{v}$ holding the molten salt of interest, in thermal contact with a heat reservoir at the desired absolute temperature T. In the interests of simplicity, for the present, we shall suppose that $\mathcal{v}$ and T correspond to a single liquid phase (Sec. VII is concerned with the heterogeneous case). It is convenient to assume that the walls of the containing vessel may be idealized as infinitely high and steep potential barriers.