# Theory of Fused Salts*†

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The properties of ionic pair distributions are investigated for a simple fused-salt model. The short-range ion core forces are assumed to be identical for both anions and cations and, although the method is capable of handling mixtures of ions with different charges, only a single fused salt of the symmetrical-valence type is considered. A set of relations is developed to describe the asymptotic behavior (for large ion distances) of the ion pair distribution functions. These relations are obtained with benefit only of certain weak, plausible assumptions concerning the triplet superposition defects; as a consequence, the usual superposition approximation of liquid theory is circumvented. A significant feature of the results is prediction of concentric shells of average charge density surrounding a given ion in a manner suggesting local latticelike structure.

## I.

IN this article we propose a simple model for understanding the equilibrium behavior of fused salts. The following analysis is perhaps of rather general interest in that, by slight elaboration, the technique outlined here may be adapted to handle concentrated electrolytic solutions. The important fact to be stressed in the following is that the ion Coulomb interactions, as well as the core interactions, are each equally influential in determining the characteristics of the fused salt near its melting point. Thus, for example, the short-range repulsive forces effectively provide geometrical constraints on the possible ion positions, resulting at least locally in a sort of close-packed latticelike structure; simultaneously, the electrostatic forces try to pair off ions of opposite charge. It is found that the result of these competing tendencies is to surround a given ion on the average by concentric shells of alternating charge density, similar to the charge ordering in ionic crystals where successive shells of neighbors differ in sign.

By varying the Coulombic coupling between the ions in a canonical ensemble, a set of integral equations is derived for determination of the fused-salt ion distributions. The central result of the following analysis is a linear inhomogeneous integrodifferential equation satisfied exactly by a function which alone determines the ion pair distributions at large separations. Granted certain reasonable hypotheses concerning the deviation from superposability of triplet potentials of mean force, it is significant that our results do not hang upon the restrictive principle of superposition as it is often used in the molecular theory of fluids.

The manner is quite clear in which the Debye-Hückel limiting theory is obtained at extremely high temperatures (or low ion number densities) in terms of our expressions for ionic distribution. Extension to larger values of the Debye-Hückel parameter $\kappa$ necessarily involves in complicated fashion details of the short-range ion interactions.

## II.

The fused salt to be considered will be restricted to the symmetrical-valence type, so that individual ions bear a small integral multiple ($\pm z$) of the electronic charge $e$. Furthermore, the total potential of interaction $V_N$ for the assembly of $N$ ions in a suitable container of volume $\mathcal{U}$ will be taken as pairwise additive

$$V_N = \sum_{i<j=1}^{N} V_{ij}. \qquad (1)$$

Two contributions to each $V_{ij}$ may immediately be distinguished, each of which we will take to be centrally symmetric[1]:

$$V_{ij}(r) = V_{ij}^{(0)}(r) + V_{ij}^{(1)}(r). \qquad (2)$$

$V_{ij}^{(0)}$ represents the potential of short-range forces acting between the ion cores; its most noteworthy feature insofar as fused salts are concerned is inclusion of a strong repulsion at small distances $r$, reflecting improbability of ion interpretation. A reasonable choice for $V_{ij}^{(0)}$ would be at least qualitatively similar to the Lennard-Jones potentials often used to represent

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[1] The pairwise additive and central form of the total short-range interaction

$$V_N^{(0)} = \sum_{i<j=1}^{N} V_{ij}^{(0)}(r_{ij})$$

may be generalized somewhat without changing the following analysis. It is only necessary to demand, for a fixed set of $N$ ion positions, that $V_N^{(0)}$ be invariant under the replacement of cations for anions, and vice versa. For present purposes this generalization is unimportant; a pairwise $V_N^{(0)}$ has the advantage of being easy to visualize.

interactions of noble gas atoms (which might be re-garded as discharged ion cores). $V_{ij}^{(1)}$ is the Coulomb potential[2]:

$$V_{ij}^{(1)}(r) = \xi_i \xi_j [(ze)^2 / Dr]. \tag{3}$$

The charging parameters $\xi_i$, $\xi_j$ are $+1$ and $-1$ for cations or anions, respectively. Since the system as a whole is electrically neutral, the number of cations $N_+$ is equal to the number of anions $N_-$; equivalently,

$$\sum_{i=1}^{N} \xi_i = 0, \qquad N = N_+ + N_-. \tag{4}$$

For the sake of mathematical convenience, we wish to restrict the fused salt model to having the simplest possible characteristics consistent with the general picture of ionic fluids. With this point of view, we demand that the potentials $V_{ij}^{(0)}$ be identical functions of $r$ for all ion pairs.[1] At least as far as the notion of ionic radii is concerned, this condition is rather closely obeyed by salts such as KF, CsCl, and BaO. The sig-nificance of deviation from this ideal in the case of other salts is lessened by the fact that ion core interactions come most strongly into play between ions of opposite charge on account of Coulombic attraction. Assuming $V_{ij}^{(0)}$ to be this anion-cation potential will thereby minimize possible error.

The ultimate object of the following investigation will be an analysis of the fluid's macroscopic properties by means of ionic distribution functions. The result of the preceding remarks is that our simple model has been constrained to possess complete charge symmetry. There are consequently just two independent ion pair correlation functions to be determined[3]:

$$g_{++}^{(2)}(r) = g_{--}^{(2)}(r),$$

$$g_{+-}^{(2)}(r) = g_{-+}^{(2)}(r), \tag{5}$$

which suffice to compute the fused salt thermodynamic functions as well as the x-ray scattering pattern. The first of Eqs. (5), stating that the correlation between pairs of cations and of anions is the same, follows directly from the model charge symmetry. The second relation (5) reflects isotropy of the fluid salt medium in the absence of external forces.

The correlation function $g_m(r)$ for particles of any type at a radial distance $r$ from either a central anion or cation, is just the arithmetic mean of $g_{++}^{(2)}(r)$ and $g_{+-}^{(2)}(r)$,

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

$$= \tfrac{1}{2}[g_{-+}^{(2)}(r) + g_{--}^{(2)}(r)]. \tag{6}$$

Notice that whereas two like ions at a given distance of separation $r$ might experience a mean repulsion, unlike ions would be expected to exhibit a mean attraction by virtue of charge sign change. The average correlation $g_m(r)$ consequently will show less fluctuation about unity than either $g_{++}^{(2)}(r)$ or $g_{+-}^{(2)}(r)$. Stated in another way, this amounts to concluding that the ionic charges (by virtue of the extreme range of Coulomb forces) will induce at fairly large distances fluctuations in the anionic and cationic number densities *relative to each other*, but that it is only in the immediate vicinity of a given ion that the *total* density varies. On this basis it is postulated that $g_m(r)$ approaches its asymp-totic limit unity much more rapidly than do either $g_{++}^{(2)}(r)$ or $g_{+-}^{(2)}(r)$. In a later section, $g_m(r)$ will in fact be identified with the correlation function in a single-component fluid whose particles interact with only forces of considerably shorter range than the Coulomb forces.

A new function $\phi(r)$ is defined by the ratio

$$g_{++}^{(2)}(r) / g_{+-}^{(2)}(r) = \exp[-2\phi(r)/kT]. \tag{7}$$

$2\phi(r)$ is therefore the mean reversible work (at absolute temperature $T$) required to take an anion, at distance $r$ from a cation, to "infinity" (though still within the fused salt medium), and subsequently to bring another cation in from "infinity" to the original position. For convenience in presentation, it is preferable to regard $g_m(r)$ and $\phi(r)$ as the two independent functions to be determined, rather than $g_{++}^{(2)}(r)$ and $g_{+-}^{(2)}(r)$. By solving (6) and (7), it is found that

$$g_{++}^{(2)}(r) = \frac{2g_m(r)}{\exp[2\phi(r)/kT]+1},$$

$$g_{+-}^{(2)}(r) = \frac{2g_m(r)\,\exp[2\phi(r)/kT]}{\exp[2\phi(r)/kT]+1}. \tag{8}$$

We note in passing that the average electrostatic charge densities, $\rho_+^{(el)}(r)$ and $\rho_-^{(el)}(r)$ surrounding cations and anions are just

$$\rho_+^{(el)}(r) = -\rho_-^{(el)}(r)$$

$$= (ze)(N_+/\mathcal{V})g_{++}^{(2)}(r) - (ze)(N_-/\mathcal{V})g_{+-}^{(2)}(r)$$

$$= -2zecg_m(r)\,\tanh[\phi(r)/kT],$$

$$c = N_+/\mathcal{V} = N_-/\mathcal{V}. \tag{9}$$

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[2] Note here that the difficult problem of determining the appro-priate dielectric constant D from individual ion polarizabilities is avoided. The form (3) will be regarded as an inherent charac-teristic of the fused salt model. Any deviations from the asymp-totic dielectric constant D when r is small may be absorbed in $V_{ij}^{(0)}$. In practical cases, D will be estimated from the refractive index.

[3] For a comprehensive account of the elements of molecular distribution function theory see T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 6.

These charge densities are subject to local electro-neutrality conditions, whereby the total average charge surrounding any ion must exactly counteract that ion's own charge. Therefore, $g_m(r)$ and $\phi(r)$ must satisfy the relation,

$$1/8\pi c = \int_0^\infty r^2 g_m(r) \tanh[\phi(r)/kT]dr. \quad (10)$$

The problem is to develop further relations between $g_m(r)$ and $\phi(r)$ from the fundamentals of statistical mechanics, since (10) alone is trivial and not particularly informative. For this purpose a coupling parameter technique is useful, wherein the electrostatic charge on one of the ions (chosen arbitrarily as ion 1) is allowed to vary continuously. Only at the end of our computation will it be necessary to set this ionic charge equal to its actual "physical" value $\pm ze$. This charging process is accomplished by considering changes in the parameter $\xi_1$.[4]

In the petit canonical ensemble theory, the $n$th-order fluid correlation functions $g^{(n)}$ and potentials of mean force $W^{(n)}$ are expressed as an integral of the canonical configuration density over the remaining $N-n$ particle positions,

$$g_{1\beta\cdots\nu}^{(n)}(\xi_1) = \exp\{-[W_{1\beta\cdots\nu}^{(n)}(\xi_1)]/kT\}$$

$$= \mathcal{V}^n \int_{\mathcal{V}} \cdots \int_{\mathcal{V}} \exp\{(kT)^{-1}[A_N(\xi_1)$$

$$- V_N(\xi_1)]\}d\mathbf{r}_{n+1}\cdots d\mathbf{r}_N, \quad \beta\cdots\nu = +, -, \quad (11)$$

where certain terms of negligible order $1/N$ have been disregarded. Here we have indicated explicitly only the dependence upon the parameter $\xi_1$. $A_N$ is the normalizing factor,

$$\exp[-A_N(\xi_1)/kT]$$

$$= \int_{\mathcal{V}} \cdots \int_{\mathcal{V}} \exp[-V_N(\xi_1)/kT]d\mathbf{r}_1\cdots d\mathbf{r}_N. \quad (12)$$

A differentiation with respect to $\xi_1$ of the logarithm of Eq. (11) for $n=2$, followed by rearrangement and subsequent integration over $\xi_1$, leads to the integral equation,

$$W_{1\beta}^{(2)}(r_{12}, \xi_1) - W_{1\beta}^{(2)}(r_{12}, 0)$$

$$= \xi_1\xi_2[(ze)^2/Dr_{12}] + \sum_{\gamma=+,-} \xi_3 c \int_0^{\xi_1} d\xi_1' \int_{\mathcal{V}} d\mathbf{r}_3$$

$$\times [(ze)^2/Dr_{13}]g_{1\gamma}^{(2)}(r_{13}, \xi_1')$$

$$\times \left\{ \exp\left[ -\frac{W_{\beta\gamma}^{(2)}(r_{23})}{kT} - \frac{\epsilon_{1\beta\gamma}^{(3)}(123, \xi_1')}{kT} \right] - 1 \right\}. \quad (13)$$

The $d\mathbf{r}_3$ integration is over all positions of a third ion of type $\gamma$ ($\xi_3 = +1$ if $\gamma = +$, $\xi_3 = -1$ if $\gamma = -$). The superposition defect function $\epsilon^{(3)}$ measures the extent to which triplet potentials of mean force may be represented by a sum of the three appropriate mean pair potentials,

$$\epsilon_{\alpha\beta\gamma}^{(3)}(123) = W_{\alpha\beta\gamma}^{(3)}(123) - W_{\alpha\beta}^{(2)}(r_{12})$$

$$- W_{\alpha\gamma}^{(2)}(r_{13}) - W_{\beta\gamma}^{(2)}(r_{23}). \quad (14)$$

One approach to the theory of liquids is to obtain a closed set of equations for pair distributions by supposing all the $\epsilon^{(3)}$ to vanish; it will be seen that in the present context this hypothesis is unnecessarily stringent. $W_{1\beta}^{(2)}(r_{12}, 0)$ in (13) is the potential of mean force acting between a fully charged ion of type $\beta$, and the completely discharged ion 1; it is of course the same for $\beta$ either $+$ or $-$.

Set $\beta$ successively equal to $+$ and $-$ in (13), and let the difference of the results define $\phi(r_{12}, \xi_1)$ [in Eq. (7) we have already introduced $\phi(r_{12}) \equiv \phi(r_{12}, 1)$],

$$2\phi(r_{12}, \xi_1) = W_{1+}^{(2)}(r_{12}, \xi_1) - W_{1-}^{(2)}(r_{12}, \xi_1)$$

$$= 2\xi_1[(ze)^2/Dr_{12}] + [c(ze)^2/D]\int_0^{\xi_1} d\xi_1' \int_{\mathcal{V}} (d\mathbf{r}_3/r_{13})$$

$$\times \left\{ g_{1+}^{(2)}(13, \xi_1') \left[ \exp\left( -\frac{W_{++}^{(2)}(23)}{kT} - \frac{\epsilon_{1++}^{(3)}(123, \xi_1')}{kT} \right) \right.\right.$$

$$\left. - \exp\left( -\frac{W_{-+}^{(2)}(23)}{kT} - \frac{\epsilon_{1-+}^{(3)}(123, \xi_1')}{kT} \right) \right]$$

$$+ g_{1-}^{(2)}(13, \xi_1') \left[ \exp\left( -\frac{W_{--}^{(2)}(23)}{kT} - \frac{\epsilon_{1--}^{(3)}(123, \xi_1')}{kT} \right) \right.$$

$$\left.\left. - \exp\left( -\frac{W_{+-}^{(2)}(23)}{kT} - \frac{\epsilon_{1+-}^{(3)}(123, \xi_1')}{kT} \right) \right] \right\}. \quad (15)$$

The potentials of mean force $W_{\alpha\beta}^{(2)}(r_{12})$ have the property of becoming small as the distance $r_{12}$ between ions 1 and 2 becomes large. Furthermore, the superposition defect function $\epsilon_{\alpha\beta\gamma}^{(3)}(123)$ decreases to zero when any one of $r_{12}, r_{13}, r_{23}$ becomes large.[5] On the basis of these considerations, the asymptotic form of Eq. (15) is obtained, for large $r_{12}$, by linearizing the integrand with respect to the $\epsilon^{(3)}$'s. When $g_m(r_{13}, \xi_1')$ is defined in analogy to Eq. (6), we find that the large $r_{12}$

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[4] Violation of the over-all electroneutrality condition (4) to the extent of small arbitrary variations in $\xi_1$ may be disregarded, since the system has macroscopic size.

[5] One is not justified in assuming, however, that the rate of decrease to zero of $\epsilon^{(3)}$ with an increasing ion pair distance is of higher order than the corresponding decrease of $W^{(2)}$.

form of (15) is

$$\phi(r_{12}, \xi_1) = \xi_1[(ze)^2/Dr_{12}] - E(r_{12}, \xi_1)$$

$$+ [c(ze)^2/D] \int_0^{\xi_1} d\xi_1' \int_{\mathcal{V}} (d\mathbf{r}_3/r_{13}) g_m(r_{13}, \xi_1')$$

$$\times \left\{ \exp\left[ -\frac{W_{++}{}^{(2)}(23)}{kT} \right] - \exp\left[ -\frac{W_{+-}{}^{(2)}(23)}{kT} \right] \right\}$$

$$E(r_{12}, \xi_1) = [c(ze)^2/2DkT] \int_0^{\xi_1} d\xi_1' \int_{\mathcal{V}} (d\mathbf{r}_3/r_{13})$$

$$\times \left\{ g_{1+}{}^{(2)}(r_{13}, \xi_1') \left[ \exp\left( -\frac{W_{++}{}^{(2)}(23)}{kT} \right) \epsilon_{1+}{}_+{}^{(3)}(123, \xi_1') \right. \right.$$

$$\left. - \exp\left( -\frac{W_{+-}{}^{(2)}(23)}{kT} \right) \epsilon_{1-}{}_+{}^{(3)}(123, \xi_1') \right]$$

$$+ g_{1-}{}^{(2)}(r_{13}, \xi_1') \left[ \exp\left( -\frac{W_{++}{}^{(2)}(23)}{kT} \right) \epsilon_{1-}{}_-{}^{(3)}(123, \xi_1') \right.$$

$$\left. \left. - \exp\left( -\frac{W_{+-}{}^{(2)}(23)}{kT} \right) \epsilon_{1+}{}_-{}^{(3)}(123, \xi_1') \right] \right\}$$

$$g_m(r_{13}, \xi_1') = \tfrac{1}{2}[g_{1+}{}^{(2)}(r_{13}, \xi_1') + g_{1-}{}^{(2)}(r_{13}, \xi_1')]. \quad (16)$$

We have made use of the identities,

$$W_{++}{}^{(2)}(23) = W_{--}{}^{(2)}(23),$$

$$W_{+-}{}^{(2)}(23) = W_{-+}{}^{(2)}(23), \quad (17)$$

consistent with Eqs. (5).

It is now asserted that $E(r_{12}, \xi_1)$ vanishes more strongly, as $r_{12}$ increases, than does $\phi(r_{12}, \xi_1)$. The conditions on the several $\epsilon^{(3)}$'s which ensure this behavior of $E(r_{12}, \xi_1)$ are discussed in the Appendix. The implication, so far as the asymptotic Eq. (16) is concerned, is that $E(r_{12}, \xi_1)$ may be dropped without destroying the validity of that relation

$$\phi(r_{12}, \xi_1) = \xi_1[(ze)^2/Dr_{12}] + \xi_1[c(ze)^2/D]$$

$$\times \int_{\mathcal{V}} (d\mathbf{r}_3/r_{13}) g(r_{13}, \xi_1) \left\{ \exp\left[ -\frac{W_{++}{}^{(2)}(23)}{kT} \right] \right.$$

$$\left. - \exp\left[ -\frac{W_{+-}{}^{(2)}(23)}{kT} \right] \right\}$$

$$g(r_{13}, \xi_1) = \xi_1^{-1} \int_0^{\xi_1} g_m(r_{13}, \xi_1') d\xi_1'. \quad (18)$$

The exponentials in the integrand of (18) may be linearized unless $W_{\alpha\beta}{}^{(2)}(23)$ is large, i.e., $r_{23}$ is small. But having already demanded that $r_{12}$ be large [since only asymptotic validity is claimed for (18)], this nonlinear region must have $r_{13}$ large. It has already been remarked that $g_m(r_{13}, \xi_1)$, and therefore $g(r_{13}, \xi_1)$ for large $r_{13}$ attain their asymptotic values unity very rapidly; for this reason, $g(r_{13}, \xi_1)$ is taken to be identically unity for the troublesome region of small $r_{23}$ values in (18). If, therefore, the Laplacian differential operator $\nabla_1^2$ with respect to the position of ion 1 is applied to both sides of (18), the integrand then vanishes when $r_{23}$ is small. Consequently, no error is incurred in the asymptotic equation by linearizing the exponentials for all positions of particle 3. If one uses the fact that $g(r_{13}, \xi_1)$ is spherically symmetric, (18) may be transformed into the linear integrodifferential equation $(r_{12} \gg 0)$,

$$\nabla_1^2 \phi(r_{12}, \xi_1) = -\xi_1[2c(ze)^2/DkT] \int_{\mathcal{V}} \phi(r_{23}, 1)$$

$$\times \{[g''(r_{13}, \xi_1) r_{13}] - 4\pi\delta(r_{13}) g(r_{13}, \xi_1)\} d\mathbf{r}_3. \quad (19)$$

The three-dimensional delta function arises when $\nabla_1^2$ is applied to the Coulomb interaction.

A naive way of recovering the linearized Poisson-Boltzmann equation of the Debye-Hückel theory immediately suggests itself. If the correlation function $g(r_{13}, \xi_1)$ were everywhere equal to the large $r_{13}$ value unity, (19) would simplify $(\xi_1 = 1)$

$$\nabla_1^2 \phi(r_{12}, 1) = \kappa^2 \phi(r_{12}, 1),$$

$$\kappa^2 = 8\pi c(ze)^2/DkT. \quad (20)$$

The well-known solutions to this differential equation are without significance for fused salts near their melting points. In view of the facts that fused salts have dielectric constants on the order of 3, and concentrations around 50 moles per liter, the corresponding values of $\kappa$ are enormous by comparison with typical dilute electrolytic solutions. The "diffuse" charge atmosphere around a central ion as predicted in this manner would be a thin skin of neutralizing charge only a few hundredths of an Angstrom unit thick. The ion core short-range forces implicit in $g(r_{13}, \xi_1)$ play a preeminent role in establishing the fused-salt local structure, and they must be reckoned with in considerable detail to yield even a qualitatively correct picture of the fluid.

For realistic short-range interactions, $g(r_{13}, \xi_1)$ will vanish at the origin because of the improbability of ion core interpretation. As a result, the second term of the integrand in (19) may be dropped. Because of the two-center nature of this integral, it is natural to transform to dipolar coordinates. One has, after performing an

elementary integration,

$$\chi''(R, \xi_1) = (\kappa^2/2) \int_0^\infty [g'(|R-s|, \xi_1)$$

$$-g'(R+s, \xi_1)] \chi(s, 1) ds,$$

$$\chi(R, \xi_1) = R\phi(R, \xi_1). \quad (21)$$

As before, it is justifiable to claim that the correct function $\chi$ satisfies (21) only as $R \to \infty$. By adding a suitable inhomogeneous function $h(R, \xi')$, an integrodifferential relation satisfied exactly by $\chi$ for all $R > 0$ is formally obtained,

$$\chi''(R, \xi_1) = h(R, \xi_1)$$

$$+ (\kappa^2/2) \int_0^\infty [g'(|R-s|, \xi_1) - g'(R+s, \xi_1)] \chi(s, 1) ds. \quad (22)$$

$h(R, \xi_1)$ must vanish for large $R$ more rapidly than $\chi''(R, \xi_1)$ since (22) must reduce to (21). It may be recognized that $h(R, \xi_1)$ contains contributions arising not only from the superposition defects $\epsilon^{(3)}$, but also from the nonlinear portions of Eq. (18) disregarded in passing to Eq. (19).

### III.

We proceed to construct the solutions to (22). For this purpose it is helpful to define $g'(R, \xi_1)$ to be an even function of $R$, and $h(r, \xi_1)$ to be odd. $\chi''(R, \xi_1)$ then becomes an odd function of $R$ by satisfying the resulting extension of (22) onto the negative axis

$$\chi''(R) = h(R) + (\kappa^2/2) \int_0^\infty [g'(R-s) - g'(R+s)] \chi(s) ds, \quad (23)$$

where $\xi_1$ has been set equal to the "physical" value $+1$, and the dependence of $\chi$, $h$, and $g$ on this variable has been suppressed.

The physically admissible solution $R^{-1}\chi(R)$ for the fused salt must vanish at infinity because of a similar condition on the pair potentials of mean force. It will in fact be supposed that a positive constant $\epsilon$ exists such that $\exp(\epsilon R)\chi(R)$ is bounded as $R$ increases; this exponential loss of order in pair space we shall take to be characteristic of fluids. It must be mentioned in this connection that the x-ray scattering patterns for all fluids, although clearly exhibiting maxima at certain angles, nevertheless do not show the sharp and distinctive Bragg reflections typical of crystalline solids, the latter having true long-range configurational order. A nonexponentially damped solution of (23) would yield scattering patterns of the crystalline solid, rather than the fluid, variety.

Introduce the following Fourier transforms:

$$Y_+(z) = \int_0^{+\infty} \chi''(R) \exp(izR) dR,$$

$$Y_-(z) = \int_{-\infty}^0 \chi''(R) \exp(izR) dR,$$

$$H_+(z) = \int_0^{+\infty} h(R) \exp(izR) dR,$$

$$H_-(z) = \int_{-\infty}^0 h(R) \exp(izR) dR,$$

$$j(z) = \int_{-\infty}^{+\infty} g'(R) \exp(izR) dR. \quad (24)$$

If the first, second, and last of Eqs. (24) are integrated by parts, one finds

$$Y_+(z) = -\chi'(0) + i\chi(0)z - z^2 X_+(z),$$

$$Y_-(z) = -Y_+(-z),$$

$$X_+(z) = \int_0^{+\infty} \chi(R) \exp(izR) dR,$$

$$j(z) = 2 + 2z \int_0^{+\infty} \sin(zR)[g(R) - 1] dR, \quad (25)$$

where the odd character $\chi(R)$, and the even character of $g'(R)$ have been used. In view of the condition on $\chi(R)$ at infinity already mentioned, we know that $X_+(z)$ is an analytic function of $z$ for

$$\text{Im}(z) > -\epsilon; \quad (26)$$

the same conclusion holds for $Y_+(z)$.

If $A$ is the largest positive constant for which $\exp(AR)[g(R)-1]$ is bounded as $R \to +\infty$, then $j(z)$ is analytic in the strip

$$-A < \text{Im}(z) < +A. \quad (27)$$

By virtue of our former observations concerning the asymptotic nature of $g(R)$ as contrasted with the corresponding behavior of the ionic correlation functions, we may suppose that $A > \epsilon$. The integrodifferential Eq. (23) is therefore equivalent to

$$\int_{-\infty+i\lambda}^{+\infty+i\lambda} [Y_-(z) - H_-(z) + (\kappa^2/2)j(z)X_+(-z)]$$

$$\times \exp(-iRz) dz$$

$$+ \int_{-\infty+i\mu}^{+\infty+i\mu} [Y_+(z) - H_+(z) - (\kappa^2/2)j(z)X_+(z)]$$

$$\times \exp(-iRz) dz = 0,$$

$$-A < \lambda < +\epsilon, \quad -\epsilon < \mu < +A. \quad (28)$$

Appealing to a well-known theorem concerning Fourier transforms,[6] we write for the entire strip (27),

$$[Y_-(z)-H_-(z)+(\kappa^2/2)j(z)X_+(-z)]$$
$$+[Y_+(z)-H_+(z)-(\kappa^2/2)j(z)X_+(z)]=0; \quad (29)$$

the content of each square bracket is itself analytic in this strip. Insert the results (25) for $Y_+$ and $Y_-$ in (29) to obtain

$$X_+(z)-X_+(-z)=\frac{2i\chi(0)z-H_+(z)-H_-(z)}{z^2+(\kappa^2/2)j(z)}. \quad (30)$$

The combination $X_+(z)+X_+(-z)$ is the Fourier transform of the odd extension onto the negative real axis of a function defined on the positive axis; since $\chi(R)$ has already been defined to be odd, this difference is just the transform of $\chi(R)$ itself. The inversion integral immediately yields $\chi(R)$

$$\chi(R)=(1/2\pi)\int_{-\infty}^{+\infty}\frac{2i\chi(0)z-H_+(z)-H_-(z)}{z^2+(\kappa^2/2)j(z)}$$
$$\times\exp(-iRz)dz. \quad (31)$$

The arbitrary constant $\chi(0)$ corresponds to the complementary solution of the homogeneous integro-differential equation, and its value must eventually be determined by satisfying the local electroneutrality condition (10).

The general solution to the integrodifferential Eq. (23), besides the function (31), will contain solutions of the homogeneous equation of the form,

$$\chi_n(R)=\exp(iz_nR)-\exp(-iz_nR), \quad (32)$$

where the complex numbers $z_n$ satisfy

$$d(z_n)\equiv z_n^2+(\kappa^2/2)j(z_n)=0 \quad (33)$$

and

$$-A<\mathrm{Im}(z_n)<+A. \quad (34)$$

That each $\chi_n(R)$ is in fact such a solution may be easily verified by substitution. However, since the $\chi_n(R)$ fail to satisfy the condition of vanishing exponentially at infinity, they cannot be included in constructing physically meaningful fluid correlation functions.

The desired solution $\chi(R)$ is therefore given alone by the contour integral (31) which, upon closing the contour along the appropriate infinite semicircle, may be evaluated by the calculus of residues. When $R>0$, $\chi(R)$ has the form

$$\chi(R)=\sum_k A_k\exp(-iz_kR),$$

$$A_k=i\lim_{z\to z_k}\left[(z-z_k)\frac{2i\chi(0)z-H_+(z)-H_-(z)}{z^2+(\kappa^2/2)j(z)}\right]. \quad (35)$$

The summation covers the poles $z_k$ of the integrand of (31) in the lower half-plane, and the constants $A_k$ are related as shown in the usual way to the residues at these poles. Among the $z_k$ are the roots of the transcendental Eq. (33). Since the inhomogeneous function $h(R)$ is known to drop to zero rapidly with increasing $R$, any poles of $H_+(z)$ and $H_-(z)$ $[=-H_+(-z)]$ remain well off the real axis; the contribution of the corresponding terms in (35) therefore dies to zero rapidly. One anticipates, therefore, that the large $R$ form of $\chi(R)$ arises from a root of (33) nearer the real axis. For these values of $R$, the inhomogeneous function $h(R)$ is in evidence only in establishing the proper values of the multiplicative constants $A_k$.

When the Debye-Hückel parameter $\kappa$ is sufficiently small, all of the roots of (33) have nonvanishing imaginary parts, so that (35) gives a properly damped $\chi(R)$. By examining the expression (25) for $j(z)$, it becomes clear that the denominator $d(z)$ always has the roots $\pm i\kappa$ in the limit $\kappa\to0$. $\chi(R)$ behaves asymptotically in this limit as $\exp(-\kappa R)$, so that the Debye-Hückel limiting theory has again been identified. Now, though, we see that this result is independent of the exact nature of $g(R)$, and therefore of the short-range ion forces.

As $\kappa$ increases (corresponding, for example, to a decrease in temperature of the fused salt at constant density), the poles of the integrand in (31) due to the roots of $d(z)$ tend to move onto, and collect along, the real axis.[7] Under this circumstance it is mandatory to adopt the principle value definition of the contour integral (31) to insure that $\chi(R)$ remain an odd function of $R$, and a smooth function of $\kappa$ (so long as the salt remains in a single fluid phase). The terms in the sum (35) corresponding to these poles along the real axis appear to give undamped contributions to $\chi(R)$, in contradiction to our condition on this function at $R=+\infty$. In addition, it may be shown that such contributions would give rise to Bragg-like x-ray scattering reflections.[8] It is necessary, as a consequence to recognize that $A_k$ must vanish as $z_k$ becomes real, to remove these spurious terms in $\chi(R)$. So far as (31) is concerned, we may infer that for each real $z_k$,

$$2i\chi(0)z_k-H_+(z_k)-H_-(z_k)=0. \quad (36)$$

Preliminary calculations on the remaining members of the sum (35) indicate that $\chi(R)$ oscillates in sign (and of course decays to zero), with a period roughly comparable to the nearest neighbor distance. By referring to the mean electrostatic charge densities $\rho_+^{(el)}(R)$ and $\rho_-^{(el)}(R)$, (9), it can be seen that every ion is surrounded on the average by concentric spherical shells of alternating sign. This characteristic un-

[6] E. C. Titchmarsh, *Introduction to the Theory of Fourier Integrals* (Oxford University Press, New York, 1950), p. 255.

[7] This typical behavior has already been noted and discussed in a similar computation in J. G. Kirkwood and J. C. Poirier, J. Phys. Chem. **58**, 591 (1954).

[8] P. J. Wojtowicz, unpublished thesis, Yale University, 1956.

doubtedly corresponds to a local ordering of the ions in a "smeared out" lattice type of structure similar to the lower temperature solid phase. In the latter as well, each ion has shells of neighbors of alternating charge.

## IV.

The "hybrid" correlation function $g_m$ has already been regarded as showing little of the rather long-ranged order induced by the ionic charges. By adapting some of the ideas of order-disorder theory,[9] we shall now find that it is possible to estimate $g_m$ as the pair correlation function in a single-component fluid, the dominant part of whose particle interactions is just $V_N^{(0)}$.

In view of Eq. (11) and the last of Eqs. (16), $g_m(r, \xi_1)$ may be written as

$$g_m(r_{10}, \xi_1) = [\mathcal{U}^2/(N-1)] \sum_{i=2}^{N} \int_{\mathcal{U}} \cdots \int_{\mathcal{U}}$$

$$\times \exp\left[\frac{A_N(\xi_1) - V_N(\mathbf{r}_1 \cdots \mathbf{r}_N, \xi_1)}{kT}\right]$$

$$\times \delta(\mathbf{r}_i - \mathbf{r}_0) d\mathbf{r}_2 \cdots d\mathbf{r}_N, \quad (37)$$

to within terms of entirely negligible order. The delta function in the integrand of (37) constrains each ion of the set $2 \cdots N$ to occupy in turn a position $\mathbf{r}_0$ at distance $r_{10}$ from the variably charged ion 1. In the configuration integrations, not only are the positions of the remaining $N-2$ ion centers variable, but for a fixed set of such positions, the cations and anions may be distributed in a large number of distinct ways. Let us therefore perform first a thermal average over the various ways of occupying the $N-1$ sites at $\mathbf{r}_2 \cdots \mathbf{r}_N$, and subsequently carry out the configuration integrations. It is by means of this artifice that the temperature dependent "potential" $\Psi_N$ is introduced by the average, over the various modes of occupation, of $\exp[-(V_N/kT)]$.

$$\exp[-(kT)^{-1}\Psi_N(\mathbf{r}_1 \cdots \mathbf{r}_N, \xi_1, T)]$$

$$= [N_c! N_a!/(N_c+N_a)!] \sum_{\xi_2 \cdots \xi_N = \pm 1}'$$

$$\times \exp[-(kT)^{-1} V_N(\mathbf{r}_1 \cdots \mathbf{r}_N, \xi_1 \cdots \xi_N)]. \quad (38)$$

The summation $\sum'$ is subject to the restriction[4]

$$\sum_{i=2}^{N} \xi_i = 0, \quad (39)$$

and $N_c$ and $N_a$ denote the number of cations and anions among the members of the set of ions $2 \cdots N$. After the

averaging operation (39), the positions $\mathbf{r}_2 \cdots \mathbf{r}_N$ are all equivalent in the sense that $\Psi_N$ is invariant to interchange of any pair of them. Accordingly, each term of the sum (37) becomes identical when (38) is employed, so that

$$g_m(r_{12}, \xi_1) = \mathcal{U}^2 \int_{\mathcal{U}} \cdots \int_{\mathcal{U}}$$

$$\times \exp\left[\frac{A_N(\xi_1) - \Psi_N(\mathbf{r}_1 \cdots \mathbf{r}_N, \xi_1, T)}{kT}\right] d\mathbf{r}_3 \cdots d\mathbf{r}_N,$$

$$\exp[-A_N(\xi_1)/kT] = \int_{\mathcal{U}} \cdots \int_{\mathcal{U}}$$

$$\times \exp\left[-\frac{\Psi_N(\mathbf{r}_1 \cdots \mathbf{r}_N, \xi_1, T)}{kT}\right] d\mathbf{r}_1 \cdots d\mathbf{r}_N. \quad (40)$$

When these last expressions are compared with the definitions (11), we conclude that $g_m$ is exactly the correlation function in a system of $N$ particles whose interaction potential is $\Psi_N$. These particles are all identical excepting particle 1 (it would be like the others if $|\xi_1| = 1$).

A differential equation for $\Psi_N$ follows directly from the definition of this quantity in (38),

$$\frac{\partial(\Psi_N(\xi_1, T)/kT)}{\partial(1/kT)} = \langle V_N(\xi_1) \rangle,$$

$$\langle V_N(\xi_1) \rangle = V_N^{(0)} + [(ze)^2/D] \sum_{i<j=1}^{N} r_{ij}^{-1} \langle \xi_i \xi_j \rangle,$$

$$\langle f \rangle = \frac{\sum_{\xi_2 \cdots \xi_N = \pm 1}' f \exp[-V_N(\xi_1 \cdots \xi_N)/kT]}{\sum_{\xi_2 \cdots \xi_N = \pm 1}' \exp[-V_N(\xi_1 \cdots \xi_N)/kT]}. \quad (41)$$

At infinite temperature, the Coulomb forces acting between the fused-salt ions are ineffective in discriminating between arrangements of the ions over the sites $\mathbf{r}_2 \cdots \mathbf{r}_N$, i.e., the ions are randomly mixed. Each average value $\langle \xi_i \xi_j \rangle$, therefore, vanishes at infinite temperature due to equal probability of anionic and cationic occupation of neighboring sites. Consequently,

$$\Psi_N(\xi_1, T = \infty) = V_N^{(0)}, \quad (42)$$

so that $\Psi$ has reduced to precisely the ion core interaction. In view of this boundary condition, the differential equation (41) may formally be integrated,

$$\Psi_N(\xi_1, T) = V_N^{(0)} + \frac{(ze)^2 kT}{D} \sum_{i<j=1}^{N} \frac{1}{r_{ij}} \int_0^{1/kT} \langle \xi_i \xi_j \rangle_{T'} d\left(\frac{1}{kT'}\right).$$

$$(43)$$

[9] Z. W. Salsburg, P. J. Wojtowicz, and J. G. Kirkwood, J. Chem. Phys. **26**, 1533 (1957).

Each of the $N(N-1)/2$ quantities $\langle \xi_i \xi_j \rangle$ depends upon all $N$ positions $\mathbf{r}_1 \cdots \mathbf{r}_N$, including of course $\mathbf{r}_i$ and $\mathbf{r}_j$ themselves. We shall, however, replace this prohibitively complicated function by its value computed for a pair of neighboring sites in the fused-salt medium, separated by distance $r_{ij}$. Roughly speaking, this procedure effectively "homogenizes" the residual discrete set of $N-2$ ion sites, since in the fused salt their positions are not fixed. Thus,

$$\langle \xi_i \xi_j \rangle \cong \frac{g_{++}^{(2)}(r_{ij}) - g_{+-}^{(2)}(r_{ij})}{g_{++}^{(2)}(r_{ij}) + g_{+-}^{(2)}(r_{ij})}$$

$$= -\tanh[\chi(r_{ij}, 1)/kTr_{ij}] \quad i, j \neq 1,$$

$$= -\xi_1 \tanh[\chi(r_{ij}, \xi_1)/kTr_{ij}] \quad i, j = 1, \quad (44)$$

where reference has been made to Eqs. (8) and (21). In this approximation, the electrostatic contribution to $\Psi_N$ is therefore a sum of centrally symmetric, pairwise additive contributions,

$$\Psi_N(\xi_1, T) = V_N^{(0)} + \sum_{j=2}^{N} \psi(r_{1j}, \xi_1) + \sum_{i<j=2}^{N} \psi(r_{ij}, 1),$$

$$\psi(r_{ij}, \xi) = -[(ze)^2 kT\xi/Dr_{ij}] \int_0^{(1/kT)}$$

$$\times \tanh[\chi(r_{ij}, \xi)/kT'r_{ij}] d(1/kT'). \quad (45)$$

The particle interactions in the fictitious single component fluid for which $g_m$ is the pair correlation function are thus nearly given by the short-range core forces supplemented by the $\psi(r_{ij})$.[10] Since $\chi$ for all temperatures in the fused-salt system is an exponentially damped function of distance, the pair interactions $\psi(r_{ij})$ also drop to zero very rapidly.[11] As a result, the correlations induced by these interactions will not possess the relatively long-range character of the ionic pair distribution functions.

As a practical matter, $g_m$ is probably determined for the most part by the ion-core potential $V_N^{(0)}$ alone, since for the high temperatures encountered in fused salts, the $\psi(r_{ij})$ will not be very large. It is $V_N^{(0)}$ which leads one to picture the ion cores as a set of rather impenetrable spheres; $V_N^{(0)}$ then effectively forces the ions into local close-packed latticelike arrangements. An approximate $g_m$, computed by taking into account only

[10] In a formal way it is a simple matter to improve the estimate (45) of $\Psi_N$. To do so, it is necessary to correct systematically for the discrete nature of the environment of the sites $\mathbf{r}_i$ and $\mathbf{r}_j$ as it affects $\langle \xi_i \xi_j \rangle$. The result of the first step in this correction procedure is to add to (45) three-body interactions, whose computation requires knowledge of the fused-salt ion triplet correlations. Their inclusion should in no way modify our conclusions regarding the qualitative nature of $g_m$.

[11] It is elementary to verify for example that if $\chi(r)$ is the Debye-Hückel result $\chi(0) \exp(-\kappa r)$, $\psi(r)$ behaves for large $r$ as $r^{-6}$.

$V_N^{(0)}$, implicitly contains the requisite geometrical restrictions on possible ion positions, and should be adequate to determine closely the ion distributions by the technique of Sec. III.

## APPENDIX

Since one has been up to the present in a position to state no more than the qualitative features of the superposition defect functions $\epsilon^{(3)}$, we shall attempt only to relate the supposed asymptotic behavior of $E(r_{12}, \xi_1)$ to a set of unproved, though not unreasonable, assumptions concerning the $\epsilon^{(3)}$. Complete justification must await future analysis of these assumptions in terms of general statistical theory.

Now since each $\epsilon^{(3)}(123)$ [like the triplet potentials of mean force $W^{(3)}$] will have an appreciable magnitude only when at least one of the three ion-pair distances $(r_{12}, r_{13}, r_{23})$ is small, there are just two significant regions of the $E(r_{12}, \xi_1)$ integration (16) to be considered (we already have made $r_{12}$ large). These are characterized by:

1. $r_{23}$ small (and hence $r_{13}$ large),
2. $r_{13}$ small (so that $r_{23}$ must be large).

The curly-bracketed portion of the integrand of $E$ in Eq. (16) reduces, in these two cases, essentially to

1. $\{ \quad \} = \exp[-W_{++}^{(2)}(23)/kT]$
$$\times [\epsilon_{1++}^{(3)}(123, \xi_1') + \epsilon_{1++}^{(3)}(123, -\xi_1')]$$
$$- \exp[-W_{+-}^{(2)}(23)/kT]$$
$$\times [\epsilon_{1-+}^{(3)}(123, \xi_1') + \epsilon_{1-+}^{(3)}(123, -\xi_1')] \quad (A1)$$

2. $\{ \quad \} = g_{1+}^{(2)}(13, \xi_1')$
$$\times [\epsilon_{1++}^{(3)}(123, \xi_1') - \epsilon_{1-+}^{(3)}(123, \xi_1')]$$
$$+ g_{1+}^{(2)}(13, -\xi_1')$$
$$\times [\epsilon_{1++}^{(3)}(123, -\xi_1') - \epsilon_{1-+}^{(3)}(123, -\xi_1')]. \quad (A2)$$

For case 1, regarding the vector $\mathbf{r}_{23}$ as fixed, it will be supposed that the quantities

$$\epsilon_{1++}^{(3)}(123, \xi_1') + \epsilon_{1++}^{(3)}(123, -\xi_1') \quad (A3)$$
and
$$\epsilon_{1-+}^{(3)}(123, \xi_1') + \epsilon_{1-+}^{(3)}(123, -\xi_1') \quad (A4)$$

each become zero faster than $\phi(r_{12}, \xi_1')$ as the vector $\mathbf{r}_{12}$ increases in length. Case 2 suggests one assume (for fixed $\mathbf{r}_{13}$ now) that the combinations

$$g_{1+}^{(2)}(13, \xi_1') \epsilon_{1++}^{(3)}(123, \xi_1')$$
$$+ g_{1+}^{(2)}(13, -\xi_1') \epsilon_{1++}^{(3)}(123, -\xi_1') \quad (A5)$$
and
$$g_{1+}^{(2)}(13, \xi_1') \epsilon_{1-+}^{(3)}(123, \xi_1')$$
$$+ g_{1+}^{(2)}(13, -\xi_1') \epsilon_{1-+}^{(3)}(123, -\xi_1') \quad (A6)$$

go to zero with increasing magnitude of $\mathbf{r}_{12}$ faster than $\phi(r_{12}, \xi_1')$. These hypotheses appear to be the weakest such set, consistent with the general ideas of molecular distributions, which will insure that $E(r_{12}, \xi_1)$ vanish more rapidly than $\phi(r_{12}, \xi_1)$, for each $\xi_1$, as $r_{12}$ becomes infinite. If, incidentally, $E(r_{12}, \xi_1)$ did not have the stated asymptotic behavior, then it would not even appear possible to deduce the Debye-Hückel theory for high temperatures.

The nature of the quantities (A3) and (A4) may be given rough interpretation. The pair of ions 2 and 3 (which are close to each other) act, from the standpoint of the far removed ion 1, as a single-charge entity. We have claimed in effect that, first, the potential of average force acting between this double ion and ion 1 is not equal to the sum of the two single ion parts (potential of average force of ions 2 and 1, and of 3 and 1). Secondly (and this is the significant point)

the excess of this double-ion effect over the sum of its separate ion effects is nearly opposite for opposite charges on ion 1. Therefore, at large distances $r_{12}$, the pairs of terms in (A3) and (A4) tend to cancel.

As regards (A5) and (A6), a similar crude interpretation may be drawn. Now, though, ions 1 and 3 are in close proximity (constituting the double ion), and ion 2 is isolated. Since ion 1 may have either charge $+\xi_1'ze$ or $-\xi_1'ze$, the double ion may have either greater, or less, total charge than ion 3 alone. The occurrence probabilities of charges $+\xi_1'ze$ and $-\xi_1'ze$ on ion 1 in the neighborhood of cation 3 are of course governed by $g_{1+}^{(3)}(13, \xi_1')$ and $g_{1+}^{(2)}(13, -\xi_1')$, respectively. (A5) and (A6) state that the superposition defect averaged over the two possible compositions of the double ion drops to zero sufficiently fast. Again it is presumed that at large $r_{12}$ the pairs of terms in each of (A5) and (A6) cancel.