

Furthermore, we may suppose that the coupling with the heat bath is negligibly small, which amounts to insisting that the rate of heat flow in or out of the system for a given temperature difference between bath and system is finite, but insignificantly small. Here, we wish only to acknowledge the existence of a mechanism for thermal equilibration, without unduly influencing the structure of the system of interest. In any event, the bulk properties of the molten salt are not expected to depend in any way on the constitution of the vessel walls.

By virtue of the heat exchange mechanism between fused salt system and thermostat, the energy content of the system of ions will fluctuate from time to time, rather than be conserved, as would be the case for an isolated system. At any instant in time, the probability of finding the  $N$  ions of the salt respectively at positions  $\mathbf{r}_1 \dots \mathbf{r}_N$  with momenta  $\mathbf{p}_1 \dots \mathbf{p}_N$ , is given by the normalized Gibbs canonical phase space density function\* (50):

$$P^{(N)}(\mathbf{r}_1 \dots \mathbf{p}_N) = \frac{1}{h^{3N} \prod_{\alpha=1}^{\mu} N_{\alpha}!} \exp \left\{ \frac{1}{kT} \left[ A_N - \sum_{j=1}^N \frac{p_j^2}{2m_j} - V_N(\mathbf{r}_1 \dots \mathbf{r}_N) \right] \right\} \quad (24)$$

Here,  $k$  is Boltzmann's constant,  $h$  Planck's constant, and  $m_j$  the mass of ion  $j$ . The normalization constant  $A_N$  may be identified as the Helmholtz free energy,

$$Q_N = \exp \left\{ - \frac{A_N}{kT} \right\} = \frac{1}{h^{3N} \prod_{\alpha=1}^{\mu} N_{\alpha}!} \times \int d^3\mathbf{r}_1 \dots d^3\mathbf{p}_N \exp \left\{ - \frac{1}{kT} \left[ \sum_{j=1}^N \frac{p_j^2}{2m_j} + V_N \right] \right\} \quad (25)$$

In principle, therefore, prediction of all the thermodynamic properties of the system may be accomplished by computing the integral

\* This is the implicit form for  $P^{(N)}$  that must be used in the dielectric properties analysis of the preceding section. It should thus be inserted in equation 15 for complete and precise definition of the averages used there. Equation 14 is a valid identity for any  $P^{(N)}$ , but its application to fluids in thermal equilibrium requires the canonical form, 24.

25, since one has the several identities of thermodynamics yielding the average energy  $E$ , entropy  $S$ , and pressure  $p$ :

$$E = \left( \frac{\partial(A_N/kT)}{\partial(1/kT)} \right)_{\mathfrak{U}} \quad (26)$$

$$S = \frac{E - A_N}{T} \quad (27)$$

$$p = - \left( \frac{\partial A_N}{\partial \mathfrak{U}} \right)_T \quad (28)$$

As a practical matter, it is well known that integration of the phase space integral (eq. 25), the classical canonical partition function, is impossible except in certain limiting cases. Each momentum integral may immediately be performed, since it is a standard form, but the remaining configuration space portion is generally the stumbling block:

$$Q_N = \frac{1}{\prod_{\alpha=1}^{\mu} N_{\alpha}! \lambda_{\alpha}^{3N_{\alpha}}} \int_{\mathfrak{U}} d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \exp \left\{ - \frac{V_N}{kT} \right\} \quad (29)$$

where

$$\lambda_{\alpha} = \frac{h}{(2\pi m_{\alpha} kT)^{1/2}}; \quad N = \sum_{\alpha=1}^{\mu} N_{\alpha}$$

The configuration integral in equation 29 receives a contribution from each set of positions  $\mathbf{r}_1 \dots \mathbf{r}_N$  inside the container volume  $\mathfrak{U}$ . The amount contributed by a given configuration depends naturally on the potential energy of that configuration,  $V_N(\mathbf{r}_1 \dots \mathbf{r}_N)$ . In comparing the relative importance of two configurations, a reduction in temperature has the effect of increased discrimination. Accordingly, as  $T$  approaches absolute zero, only those configurations (there will be several corresponding to permutation of identical particles) in which the  $V_N$  attains its minimum value provide the value of  $A_N$  in equation 29. We know that these configurations have the  $N$  ions in a regular crystalline array, so the predicted Helmholtz free energy refers to the zero-temperature crystalline solid, which was to be expected.  $A_N$  may thus be readily found in this limiting case.

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At elevated temperatures corresponding to a liquid state of aggregation for the  $N$  particles, the still energetically most important crystalline arrangement becomes swamped by the higher energy, but vastly more numerous, less regular liquid structures. These latter typically have each particle surrounded by a shell of neighbors which, in dense liquids at any rate, form a "cage" in which the central particle will generally oscillate many times before escaping to a different location. Unlike the regular solid, though, this shell of near neighbors is neither as definite in position from the central particle, nor in the number of its constituent particles, as is the crystal near neighbor shell. The primary trouble in evaluation of equation 29 for liquids therefore resides in the fact that a rather wide range of different (but invariably complicated) configurations is important, no one of which can be claimed to predominate. Furthermore, these configurations have each particle simultaneously and strongly interacting with several others (its near neighbors, at least). The special difficulty for statistical mechanics posed by liquids is due to the fact that one can appeal neither to a structural regularity (crystalline solids) nor to only occasional encounters between the constituent particles (as is the situation in the gas phase).

There do exist reasonably straightforward techniques for roughly approximating the liquid phase configuration integral, some of which we shall review for the molten electrolyte case in Section V. In the circumstance that the interaction  $V_N$  has a special form, however, a reasonably practical alternative evaluation scheme for the thermodynamic properties of a liquid is available. In particular, it is necessary to require that  $V_N$  (aside from a position-independent additive constant) be a sum of particle pair interactions alone, as was concluded to be a feasible approximation for fused salts in Section III. With this restriction, it is possible to relate each thermodynamic property of interest to a set of quantities, ion pair correlation functions, which represent the probability of observing within the system pairs of particles of specified types, separated by a given radial distance (34,40).

Let us choose for the sake of illustration a specific pair of particles of types  $\alpha$  and  $\beta$ , and arbitrarily suppose they are numbered 1 and 2, respectively. Pick two infinitesimal volume elements inside  $\mathcal{U}$ ,  $d\mathcal{U}_1$  and  $d\mathcal{U}_2$  as shown in Figure 6. If the distance  $r_{12}$  is very large on the scale of molecular lengths, the probability that particle 1 is in  $d\mathcal{U}_1$

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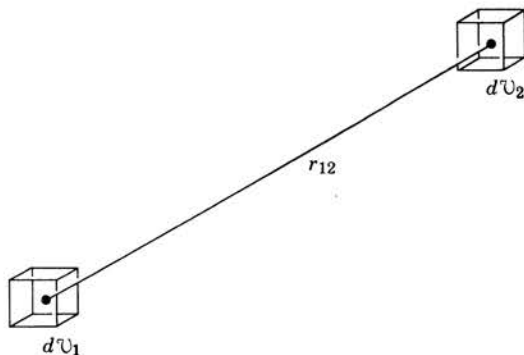


Fig. 6. Simultaneously occupied infinitesimal volume elements used in defining ion pair correlation functions.

while simultaneously 2 is in  $d\mathcal{U}_2$ , is the product of the individual occupation probabilities. That is, these are independent events if  $r_{12}$  is sufficiently large. For our macroscopic system, the joint occupation probability is, in sufficient accuracy for the present purposes, equal to

$$\frac{d\mathcal{U}_1}{\mathcal{U}} \cdot \frac{d\mathcal{U}_2}{\mathcal{U}}$$

On the other hand, if the distance  $r_{12}$  had initially been chosen small enough that particles 1 and 2 could interact by their intermolecular forces, the two occupation probabilities would no longer be independent. The probability of joint occupation must now contain a correction factor,

$$g_{\alpha\beta}^{(2)}(r_{12}) \frac{d\mathcal{U}_1}{\mathcal{U}} \cdot \frac{d\mathcal{U}_2}{\mathcal{U}} \quad (30)$$

which is conventionally named the pair correlation function.

A few general features of the  $g_{\alpha\beta}^{(2)}$  may immediately be recognized. The subscripted species types for the members of the initially chosen pair are essential, though their order is irrelevant. The intermolecular force law will differ for the various distinct types of pairs, and consequently we must anticipate that the several  $g_{\alpha\beta}^{(2)}$  are not the same. The pair correlation function as shown in expression 30 depends only on radial distance  $r_{12}$  as a result of isotropy of the homo-

geneous liquid. If one or both of the volume elements had been chosen near the walls of the container, this isotropy would be destroyed, and  $g_{\alpha\beta}^{(2)}$  would then depend on both vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . But in investigation of fused salt bulk properties, the radially symmetric pair correlation functions are sufficient. Obviously, as  $r_{12}$  becomes large,  $g_{\alpha\beta}^{(2)}(r_{12})$  must asymptotically approach unity to reproduce the original independent occupation probabilities. Furthermore, our qualitative understanding of the nature of intermolecular forces, outlined in Section II, leads us to expect each  $g_{\alpha\beta}^{(2)}(r_{12})$  to vanish as  $r_{12}$  goes to zero, owing to the essential impenetrability of particles.

The pair correlation functions for each distinct type of ion pair naturally will depend on temperature and pressure (or more conveniently, density). It is one of the main tasks of modern statistical mechanics to provide theoretical means for determining the  $g^{(2)}$ 's over the full accessible range of experimental conditions for fluids of interest. Subsequent application of the pair correlation function quadratures for thermodynamic properties, presently to be exhibited, would then represent complete solution of the statistical problem (for molten salts, in the case at hand).

The molecular, or ionic, correlation function concept may easily be generalized to sets of more than two particles. It is necessary to consider the infinitesimal volume elements  $d\mathcal{V}_1 \dots d\mathcal{V}_n$  in the requisite configuration  $\mathbf{r}_1 \dots \mathbf{r}_n$ , and to inquire then about the simultaneous occupation probability of particle 1 (type  $\alpha$ ) being in  $d\mathcal{V}_1, \dots$ , particle  $n$  (type  $\nu$ ) being in  $d\mathcal{V}_n$ . The result now will contain an  $n$ -particle correlation function,

$$g_{\alpha\beta \dots \nu}^{(n)}(\mathbf{r}_1 \dots \mathbf{r}_n) \frac{d\mathcal{V}_1}{\mathcal{V}} \cdot \frac{d\mathcal{V}_2}{\mathcal{V}} \cdot \dots \cdot \frac{d\mathcal{V}_n}{\mathcal{V}} \quad (31)$$

If each of the  $n$  volume elements is sufficiently far from the others, we may suppose that  $g^{(n)}$  reduces to unity. Within the bulk of the liquid, isotropy is reflected in the invariance of  $g^{(n)}$  to translations and rotations which preserve all volume element pair distances.

It is important to be able to provide an unambiguous mathematical definition of these correlation functions in terms of the basic notions of statistical mechanics. The complete  $N$ -particle phase space density  $P_N(\mathbf{r}_1 \dots \mathbf{p}_N)$  has already been introduced, and is given specific form by equation 24.  $g_{\alpha\beta \dots \nu}^{(n)}(\mathbf{r}_1 \dots \mathbf{r}_n)$  likewise expresses a probability, but only for the configuration coordinates of the

specified  $n$  particles, values of the other unspecified dynamical variables being irrelevant. Each  $g_{\alpha\beta\dots\nu}^{(n)}$  must therefore be obtainable from  $P^{(N)}$  by an operation which eliminates all  $N$  momenta  $\mathbf{p}_1\dots\mathbf{p}_N$ , as well as the remaining  $N-n$  positions  $\mathbf{r}_{n+1}\dots\mathbf{r}_N$ . Consistent with the fundamental ideas of probability theory, this elimination may be accomplished by integrating  $P^{(N)}$  over these parameters:

$$g_{\alpha\beta\dots\nu}^{(n)}(\mathbf{r}_1\dots\mathbf{r}_n) = \mathcal{U}^n \int P_N(\mathbf{r}_1\dots\mathbf{p}_N) d^3\mathbf{r}_{n+1}\dots d^3\mathbf{r}_N d^3\mathbf{p}_1\dots d^3\mathbf{p}_N \quad (32)$$

The additional multiplicative factor  $\mathcal{U}^n$  is necessary for normalization, to insure that  $g_{\alpha\beta\dots\nu}^{(n)}$  reduces to unity as all  $r_{ij}$  ( $1 \leq i, j \leq n$ ) increase beyond the range of intermolecular forces.

In the form shown (eq. 32), there is no readily apparent advantage to introducing the molecular correlation functions, for precisely the same integration difficulties are encountered here, for liquids, as previously in the case of the partition function itself, equation 29. A later section (VI), though, will indicate in some detail how these precise mathematical definitions may be employed to deduce practical pair correlation function calculation procedures.

Note has already been taken of the behavior of the  $g_{\alpha\beta}^{(2)}(r_{12})$  when  $r_{12}$  is very small (ion core overlap configuration) and when it is large. These functions' interesting and informative properties, however, occur at intermediate distances corresponding, roughly, to one to ten ionic diameters. If the collection of ions in our system were very dilute, so that virtually always no other ions were to be found in the vicinity of the fixed pair, 1,2, then  $g_{\alpha\beta}^{(2)}$  would be nothing more than the Boltzmann factor

$$g_{\alpha\beta}^{(2)}(r_{12}) = \exp \left[ - \frac{V_{\alpha\beta}(r_{12})}{kT} \right] \quad (33)$$

$$V_{\alpha\beta}(r_{12}) = V_{\alpha\beta}^{(s)}(r_{12}) + V_{\alpha\beta}^{(e)}(r_{12})$$

But it is especially true in the dense liquid state that the ambient medium provided by the particles neighboring 1 and 2 can modify the "bare" interaction (eq. 33). In order that the chosen pair occupy the given positions, the surrounding medium will be disrupted to some extent, and the additional  $r_{12}$ -dependent free energy required to perform the deformation modifies 33 extensively. If, for a given separation  $r_{12}$ , the requisite medium-disruption free energy is large

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and positive, the actual pair correlation function will be less than the simple Boltzmann factor (eq. 33). The proper expression replacing equation 33 at finite densities retains the Boltzmann factor form:

$$g_{\alpha\beta}^{(2)}(r_{12}) = \exp \left[ - \frac{W_{\alpha\beta}^{(2)}(r_{12})}{kT} \right] \quad (34)$$

However,  $W_{\alpha\beta}^{(2)}(r_{12})$  now includes the non-negligible medium rearrangement effects.

In dilute electrolytic fluids, it is well known that the distinction between  $V_{\alpha\beta}$  and  $W_{\alpha\beta}^{(2)}$  amounts to an exponential shielding of the Coulomb potential contained in the former; the medium disruption in this case is formation of ion atmospheres whose size is measured by the characteristic Debye length for the electrolyte. We shall later see that molten salts likewise have their own version of ion atmospheres though qualitatively in quite a different manner from the dilute electrolyte case. In any event,  $W_{\alpha\beta}^{(2)}$ , or equivalently  $g_{\alpha\beta}^{(2)}$ , must reflect sensitively the microscopic liquid structure. This fact alone would be sufficient reason to study these functions quantitatively, even if they were not useful in predicting thermodynamic properties.

If  $f(\mathbf{r}_1 \dots \mathbf{p}_N)$  is any function of the configuration coordinates and momenta for the  $N$  ions, its average value in the equilibrium state is obtained by integrating it with the phase space density  $P^{(N)}$  as a weighting factor:

$$\langle f \rangle = \frac{\int f(\mathbf{r}_1 \dots \mathbf{p}_N) P^{(N)}(\mathbf{r}_1 \dots \mathbf{p}_N) d^3\mathbf{r}_1 \dots d^3\mathbf{p}_N}{\int P^{(N)}(\mathbf{r}_1 \dots \mathbf{p}_N) d^3\mathbf{r}_1 \dots d^3\mathbf{p}_N} \quad (35)$$

A specific choice for  $f$  might be  $\mathbf{F}_1$ , the force on ion 1. This  $f$  happens to be momentum independent, and in terms of  $V_N$  is

$$\mathbf{F}_1(\mathbf{r}_1 \dots \mathbf{r}_N) = -\nabla_1 V_N(\mathbf{r}_1 \dots \mathbf{r}_N) \quad (36)$$

where  $\nabla_1$  is the gradient operator with respect to  $\mathbf{r}_1$ . If it were required to compute the mean force on particle 1 at  $\mathbf{r}_1$ , when particle 2 is held fixed at  $\mathbf{r}_2$ , a distance  $r_{12}$  away, we form the analog of equation 35 by integrating only over  $\mathbf{r}_3 \dots \mathbf{r}_N, \mathbf{p}_1 \dots \mathbf{p}_N$ .

$$\langle \mathbf{F}_1 \rangle^{(12)} = - \frac{\int (\nabla_1 V_N) P^{(N)}(\mathbf{r}_1 \dots \mathbf{p}_N) d^3\mathbf{r}_3 \dots d^3\mathbf{r}_N d^3\mathbf{p}_1 \dots d^3\mathbf{p}_N}{\int P^{(N)}(\mathbf{r}_1 \dots \mathbf{p}_N) d^3\mathbf{r}_3 \dots d^3\mathbf{r}_N d^3\mathbf{p}_1 \dots d^3\mathbf{p}_N} \quad (37)$$

where the superscript on the angular brackets indicates the fixing of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , a notation already used for similar averages in Section III, equation 15.

Now upon first taking logarithms in the definition 32, with  $n = 2$ , of  $g_{\alpha\beta}^{(2)}(r_{12})$ , we find that subsequent application of the differential operator  $\nabla_1$  to both sides, and comparison with equation 20, leads to the identification,

$$\langle \mathbf{F}_1 \rangle^{(12)} = -\nabla_1 W_{\alpha\beta}^{(2)}(r_{12}) \quad (38)$$

One therefore sees that the relation of the *average* force on particle 1, when 2 is distance  $r_{12}$  away, to  $W_{\alpha\beta}^{(2)}$  in a finite density medium, is formally the same as the pair force-pair potential relation when 1 and 2 are isolated:

$$\mathbf{F}_1(r_{12}) = -\nabla_1 V_{\alpha\beta}(r_{12}) \quad (\text{isolated pair}) \quad (39)$$

It is for this reason that  $W_{\alpha\beta}^{(2)}(r_{12})$  is called the "pair potential of mean force" acting between particles 1 and 2.

A general expression for the thermodynamic energy of a molten salt follows from application of relation 26 to the partition function, 29. In computing the relevant derivatives, it is necessary to remember that both the Born cavity energies,

$$U_{bc}^{(\alpha)}(T) \quad (40)$$

and the ion pair potentials,

$$V_{\alpha\beta}(r, T) \quad (41)$$

are functions of the temperature (at constant volume) through their dependence on dielectric constant. One readily finds

$$E = \frac{3}{2} NkT + \sum_{\alpha=1}^{\mu} N_{\alpha} \left[ U_{bc}^{(\alpha)} + \frac{1}{kT} \left( \frac{\partial U_{bc}^{(\alpha)}}{\partial (1/kT)} \right)_{\mathbf{v}} \right] \\ + \frac{1}{2} \sum_{\alpha, \beta=1}^{\mu} \frac{N_{\alpha} N_{\beta}}{\mathcal{V}} \int_0^{\infty} d^3 \mathbf{r} \left[ V_{\alpha\beta}(r) + \frac{1}{kT} \left( \frac{\partial V_{\alpha\beta}(r)}{\partial (1/kT)} \right)_{\mathbf{v}} \right] g_{\alpha\beta}^{(2)}(r) \quad (42)$$

where identical terms arising from the same types of ions, or ion pairs, have been grouped together. In this result, use has been made of the radial symmetry of each  $g_{\alpha\beta}^{(2)}$ . The integral has been extended to infinity (even though the system is finite in extent) without error for the bulk liquid energy, on account of the molten salt electroneutrality.



The factor  $1/2$  is necessary in equation 42 to prevent double counting of pairs.

A similar expression is available for the pressure in the molten salt. We shall outline an adaptation to molten salt systems of a method due to Green (28). The basic idea is simply one which allows convenient volume differentiation of the partition function to yield  $p$  by equation (28). Expression 29 for the Helmholtz free energy of the fused salt may be rewritten in the form

$$\exp \left\{ \frac{A_N^{(0)} - A_N}{kT} \right\} = \frac{1}{\mathcal{V}^N} \int \exp \left\{ - \frac{V_N}{kT} \right\} d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \quad (43)$$

where  $A_N^{(0)}$  is the ideal gas value of  $A_N$ , for  $N$  non-interacting point particles ( $V_N \equiv 0$ ). Although it is not necessary to do so, we shall suppose that the container for the system is cubical with edge length  $\mathcal{V}^{1/3}$ , and that the origin for coordinates  $\mathbf{r}_1$  to  $\mathbf{r}_N$  is located at one corner of this cube. Then the limits of integration in equation 43 for each of the  $3N$  components of the vectors  $\mathbf{r}_1 \dots \mathbf{r}_N$  (which may be denoted by  $r_{1x}, r_{1y}, r_{1z}, r_{2x}, \dots, r_{Nz}$ ) may be taken as 0 and  $\mathcal{V}^{1/3}$ .

Next, a set of dimensionless distance variables  $s_{1x} \dots s_{Nz}$  are introduced to replace the  $r$ 's:

$$\begin{aligned} r_{1x} &= \mathcal{V}^{1/3} s_{1x} \\ &\cdot \\ &\cdot \\ &\cdot \\ r_{Nz} &= \mathcal{V}^{1/3} s_{Nz} \end{aligned} \quad (44)$$

Each ion pair distance  $r_{ij}$  occurring in the detailed form of  $V_N$ , equation 23, may thereupon be expressed:

$$r_{ij} = \mathcal{V}^{1/3} [(s_{jx} - s_{ix})^2 + (s_{jy} - s_{iy})^2 + (s_{jz} - s_{iz})^2]^{1/2} \quad (45)$$

In terms of these dimensionless variables, the partition function 43, now becomes

$$\begin{aligned} \exp \left\{ \frac{A_N^{(0)} - A_N}{kT} \right\} &= \int_0^1 ds_{1x} \int_0^1 ds_{1y} \dots \int_0^1 ds_{Nz} \\ &\times \exp \left\{ - \frac{V_N(\mathbf{s}_1 \dots \mathbf{s}_N; \mathcal{V})}{kT} \right\} \end{aligned} \quad (46)$$

Computation of the pressure is now an elementary matter involving only  $\mathfrak{V}$ -differentiation under the integrals of equation 46, since the limits of integration have been freed of this parameter.

Since this differentiation is straightforward, we do not reproduce it stepwise. It is necessary to remember, though, that  $V_N$  depends on  $\mathfrak{V}$  not only because this variable occurs in expression 45 for the pair distances  $r_{ij}$ , but in addition because the dielectric properties of the melt ( $U_{bc}^{(i)}$  and  $D$ , specifically) vary as  $\mathfrak{V}$ , or equivalently the total particle density  $\rho = N/\mathfrak{V}$ , is varied. The final result is found to be:

$$\begin{aligned} \frac{p\mathfrak{V}}{NkT} &= 1 + \sum_{\alpha=1}^{\mu} \rho_{\alpha} \frac{\partial U_{bc}^{(\alpha)}}{\partial \rho} \\ &- \frac{1}{2kT} \sum_{\alpha,\beta=1}^{\mu} \rho_{\alpha}\rho_{\beta} \int d^3\mathbf{r} \left\{ \frac{r}{3\rho} \frac{\partial V_{\alpha\beta}(r)}{\partial r} - \frac{\partial V_{\alpha\beta}(r)}{\partial \rho} \right\} g_{\alpha\beta}^{(2)}(r) \quad (47) \\ \rho_{\alpha} &= \frac{N_{\alpha}}{\mathfrak{V}} \end{aligned}$$

where definition 32 of the pair correlation functions has once again been used. This result is a generalization to the case of effectively density-dependent potential energies of an equation of state formula that has been known for some time in the statistical-mechanical theory of fluids (37). In practice, it will be necessary to employ information about the density dependence of the molten salt dielectric constant, such as is provided by equation 22, to compute the pressure by equation 47.

In considering the Born cavity contribution to the molten salt pressure, the first sum on the right side of equation 47, it should be recognized that not only does the asymptotic dielectric constant  $D$  exhibit density dependence, but the effective cavity radii  $b_{\alpha}$ , in equation 20, change with  $\rho$  as well. Presumably, as a liquid is compressed, the constituent particles must settle into a more regular arrangement to utilize the lessened available volume more efficiently; the eventual result of this tendency for ordinary liquids is freezing under pressure to form the nearly perfectly regular crystal lattice. But since there is *no* Born cavity energy for lattices with each ion a center of symmetry, it is necessary to suppose each  $b_{\alpha}$  has become infinitely large by the time the ions have been forced into a regular array of this kind.

Consequently, it is reasonable to assume that  $b_\alpha$  increases as  $\rho$  increases in the liquid, as a reflection of more nearly solid-like stacking.

As a third example of pair correlation function expressions for equilibrium molten salt properties, we develop formulas for the ion chemical potentials,  $\mu_\alpha$ , for each species  $\alpha$ . Experimentally, of course, these quantities are not individually accessible, on account of the restraint of overall liquid electroneutrality. What is measurable, though, is the mean chemical potential  $\mu_\pm$ ; for an elementary salt with one anionic ( $-$ ) and one cationic ( $+$ ) species, this is

$$\rho\mu_\pm = \rho_+\mu_+ + \rho_-\mu_- \quad (48)$$

where  $\rho$  is the total particle density  $\rho_+ + \rho_-$ . In general,  $\mu_\pm$  is the number average chemical potential.

Nevertheless, the operations of statistical mechanics do allow the individual  $\mu_\alpha$ 's to be computed. They are defined to be equal to the ideal fluid chemical potential,

$$\mu_\alpha^{(0)} = kT \log \frac{N_\alpha \lambda_\alpha^3}{\mathcal{V}} \quad (49)$$

plus the amount of reversible work necessary to take a single ion of the type of interest from isolation at infinity, to the interior of the melt. This work may be split into two parts, by regarding insertion of the ion into the liquid to occur by the path:

- (a) electrostatic discharge of the ion at infinity;
- (b) insertion of the uncharged ion core into the bulk liquid, with formation of a cavity of size suitable to contain this core;
- (c) recharging of the ion to its full initial charge,  $z_\alpha e$ .

In the first and last steps, charging of the ion against its own field (the self-energy work) cancels. The cavity free energy,  $W_c^{(\alpha)}$ , in step (b) is very much like what would be encountered in computing the free energy of dissolving a noble gas atom, of size equal to the ion core, in the fused salt. Computation of  $W_c^{(\alpha)}$  is reserved for consideration in Section VII.

The extra charging work encountered in (c), compared to that for the ion *in vacuo*, (a), arises from the change in electrostatic potential at the ion's center due to the surrounding liquid. This change may be associated first with the fact that the salt is a polarizable dielectric (yielding thus a Born cavity energy for the partially charged ion),

secondly with the charge density (the fused salt "ion atmosphere") that spontaneously forms around a charging ion, and finally with the interfacial potential drop  $\psi_s$  experienced by the average electrostatic potential in crossing the interface at the system boundary. If we combine all of these contributions, the chemical potential is finally found to be

$$\begin{aligned} \mu_\alpha = & \mu_0^{(\alpha)} + W_c^{(\alpha)} + z_\alpha e \psi_s + 2 \int_0^1 \frac{d\lambda}{\lambda} U_{bc}^{(\alpha)}(\lambda) \\ & + \int_0^1 d\lambda \int d^3\mathbf{r} \frac{\lambda z_\alpha e}{Dr} \left[ \sum_{\beta=1}^{\mu} \rho_\beta z_\beta e g_{\alpha\beta}^{(2)}(r, \lambda) \right] \quad (50) \end{aligned}$$

The variable  $\lambda$  stands for the fraction of the full charge  $z_\alpha e$  on the  $\alpha$ -type ion during the charging process in the liquid. The square-bracketed sum under the second integral in equation 50 may immediately be identified as the average electrostatic charge density surrounding the partially charged central ion. Here, we have taken explicit cognizance of the fact that the pair correlation functions will generally depend upon the value of fractional charge borne by one member of the pair.

It is interesting to note that upon computing the mean chemical potential  $\mu_\pm$ , the surface potential  $\psi_s$  is entirely eliminated, by use of the electroneutrality condition,

$$\sum_{\alpha=1}^{\mu} \rho_\alpha z_\alpha = 0 \quad (51)$$

Consequently, the experimentally important chemical potential depends only on the structure of the interior of the bulk liquid, and not on the interfacial structure. Since this latter can be quite sensitive to the particular constitution of the container walls, it is reassuring that the properties of the electroneutral salt, deduced from the chemical potential expression (e.g., the liquid-vapor coexistence curve), is properly independent of the material out of which the container is made.

Among the fundamental thermodynamic quantities for the molten salt, the entropy unfortunately cannot be exhibited straightforwardly in terms of the pair correlation functions for the liquid alone. However, in view of the thermodynamic relationship,

$$dA_N = -SdT - pdV \quad (52)$$

one may obtain  $A_N$  by integration of the pressure formula (eq. 47) along an isothermal volume contraction path, starting with the ideal vapor; subsequently,  $S$  follows from temperature differentiation at constant volume. Equation 27 shows, furthermore, that  $S$  may alternatively be computed from  $A_N$ , and the energy expression 42.

For completeness, we record a final pair correlation function expression, with central importance in understanding liquid-state equilibrium structure, which provides the angular distribution of x radiation scattered from the liquid.\* For a sample in which only single scattering processes are important, the scattered intensity  $I_{sc}$  for an incident beam of intensity  $I_0$ , observed at large radial distance  $R$  from the sample, and at angle  $\theta$  to the incident direction is well known to be (assuming point radiators) (38):

$$\frac{I_{sc}(s)}{I_0} = \frac{1}{4\pi R^2} \left\{ \sum_{\alpha=1}^{\mu} N_{\alpha} A_{\alpha}^2 + \frac{1}{\mathcal{V}} \sum_{\alpha,\beta=1}^{\mu} N_{\alpha} N_{\beta} A_{\alpha} A_{\beta} \right. \\ \left. \times \int_0^{\infty} 4\pi r^2 dr \cdot \frac{\sin(sr)}{sr} [g_{\alpha\beta}^{(2)}(r) - 1] \right\} \quad (53)$$

$$s = \frac{4\pi}{\lambda_r} \sin \frac{\theta}{2}$$

The  $A_{\alpha}$ 's are ionic scattering factors, and  $\lambda_r$  is the wavelength of the radiation. The integrals occurring here are precisely three-dimensional Fourier transforms, and as such, could be uniquely inverted for liquids containing only a single molecular species, to provide an experimentally determined pair correlation function (27). For mixtures, an inversion may still be possible by combining data from both x-ray and neutron scattering experiments. In any event, theoretically predicted values of the several pair correlation functions in a molten salt can be partially checked for accuracy by insertion into equation 53, to provide comparison with the measured x-ray scattering pattern.

## V. Approximate Theories

This section is devoted to exposition of three rather distinct and independent approaches to the evaluation of the fused salt partition function. They are each designed to exploit certain features supposed

\* See chapter by H. A. Levy and M. D. Danford, this volume, p. 109.

to be exhibited in common by liquids, with a view toward allowing numerical results to be obtained for thermodynamic properties without inordinate expenditure of effort. It is remarkable that the three approaches lead to three quite different points of view about the proper picture of ion arrangements in the melt. The disparity probably reflects mainly on the present incomplete understanding of the liquid state. In developing each of these techniques, we will continue implicitly to suppose that the salt under consideration conforms to the simple pairwise additive interaction model, which has already been suggested for non-associated melts.

#### A. THE "SIGNIFICANT STRUCTURES" THEORY

In a series of publications, Eyring (18,21), Walter (70), and others have suggested an evaluation scheme to cope specifically with the difficult configuration integral occurring in the fundamental liquid (specifically, molten salt) partition function  $Q_N$ , equation 29. The resulting approximate partition function is sufficiently simple to allow ready calculation of the usual molten salt thermodynamic properties, including the melting, boiling, and critical point parameters (when these have not been employed to fix the adjustable parameters that arise). The method has had considerable success in reproducing experimental results on equations of state in the liquid region for a wide variety of substances, both electrolytic and non-electrolytic.

In the crystalline solid phase for salts at low temperatures, each ion is surrounded by a symmetrical collection of nearest neighbors, under whose confining influence the central ion undergoes harmonic vibrations about its equilibrium lattice position. In principle, it is possible as well that the ion might become displaced to a new interstitial position at which mechanical equilibrium would likewise be attained. But in order to occupy such an unnatural position, a great deal of work must be done by way of elastically distorting the lattice to accommodate the displaced particle. The number of such interstitial sites per lattice particle depends upon the specific crystal structure of the solid.

As the solid melts, at least so far as salts are concerned, there is generally observed about a 20% volume increase (8). The x-ray scattering patterns that have been observed for simple molten salts (46) demonstrate that this overall expansion is not, however, accom-

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panied by a corresponding increase in the nearest neighbor separation (the distance at which the first peak of the pair correlation functions occurs). Accordingly, it is supposed in the significant structures theory that the melting volume increase must primarily be due to introduction of a proper number of volume-consuming dislocations or imperfections in the solid structure. Of course, a variety of different lattice imperfections are possible; for monatomic liquids (such as argon) the most important are probably the vacancy, and the stacking faults that occur in failing to maintain one or the other of the close-packed lattice structures consistently in the "crystal" planes of the liquid. Such imperfections would not modify the nearest neighbor distance, but at least the former would tend to reduce the average coordination number, in qualitative agreement with the observations (46).

With the structure loosening that occurs on melting, as well as destruction of true crystalline long-range order, it is probable that the liquid-state analogs of the interstitial sites are more numerous, as well as considerably less demanding of deformation work for occupation, especially near the imperfections.

Eyring (21) quotes experimental data on gas permeability of glasses (supercooled liquids with presumably much the same structure as ordinary liquids in equilibrium) by helium in support of the contention that the "dislocations" present in the liquid state are to an important extent arranged in tunnels or passageways. Some of these, though, are probably as short as one lattice spacing (simple vacancy) and unconnected to others, so as to be undetectable in a permeability measurement. In any event, if this connectivity is the case, at least partially, it is assumed that some of the particles forming the liquid are free to "evaporate" into these passageways, and to traverse them in a gas-like manner.

The significant structures theory therefore sets itself a twofold task. The first is recognition that the translational motions of the particles may be either of two types: (1) "solid-like," for particles moving in the harmonic potential well formed by their neighbors, and (2) "gas-like," for those particles moving along the passageways in the liquid. The "significant structures" therefore are the porous pseudo-crystalline framework of harmonically bound particles, and the set of gas particles occupying the voids in this framework. The second task is formulation of a rule for dividing the total number,  $3N$ ,

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of particle translational degrees of freedom between the two modes of motion.

It is hypothesized that each particle in a solid-like site consumes no more room in the liquid than it does in the solid phase at its melting point. If the actual liquid volume is  $\mathcal{V}$ , and  $\mathcal{V}_s$  is the solid's volume at the melting point, then the fraction of the total number  $N$  of particles to be found in solid-like sites is  $\mathcal{V}_s/\mathcal{V}$ , and the remainder,  $(\mathcal{V} - \mathcal{V}_s)/\mathcal{V}$ , then must be assigned to gas-like degrees of freedom.

The procedure for constructing the approximate partition function for the liquid therefore consists in writing a product of single-particle partition functions for each particle in the solid structure, and multiplying the result by the ideal gas partition function for the remaining gas-like motions. The particles in the pseudocrystalline framework are presumed to conform to the Einstein picture of solids (20), whereby each particle is assumed to undergo harmonic oscillations about its equilibrium position. If  $n_h$  represents the number of extra "strained" sites available per particle in the solid-like structure, and  $a/n_h$  the common strain energy for those sites (thereby defining  $a$ ), the appropriate single-particle partition function factor is given by

$$Q_{\text{solid}} = \frac{\exp \{ -E_i/kT - \theta/2T \}}{(1 - \exp \{ -\theta/T \})^3} [1 + n_h \exp \{ -a/n_h kT \}] \quad (54)$$

$E_i$  is the potential energy per particle in the lattice of solid-like particles, and  $\theta$  is related to the Einstein frequency  $\bar{\nu}$  by

$$\theta = h\bar{\nu}/k \quad (55)$$

Generally, the harmonic oscillator zero-point energy  $k\theta/2$  is sufficiently small with respect to  $kT$  at molten salt temperatures, that  $\theta/2T$  in the numerator of equation 54 may be neglected.

Carlson et al. (18) take  $E_i$  to be equal to the sublimation energy,  $E_s$ , of the actual solid, times  $(\mathcal{V}_s/\mathcal{V})^{1/3}$  to account for the change in Coulomb energy for the set of ions constituting the pseudocrystalline structure, by virtue of the mean change in linear dimension upon melting. Blomgren (4), however, acknowledges the existence of both short- and long-range forces between ions, and takes

$$E_i = E_1 \left( \frac{\mathcal{V}_s}{\mathcal{V}} \right)^{1/3} + E_2 \left( \frac{\mathcal{V}_s}{\mathcal{V}} \right) \quad (56)$$



He supposes that the long-range part of  $E_1$ , the  $E_1$  term, is equal to the solid-phase Madelung energy times the ratio of liquid to solid phase near-neighbor coordination numbers ( $4/6$  for KCl, for example).  $E_2$  is then identified with a noble gas sublimation energy (argon is chosen for KCl because of similar electron structure for the constituent particles). The  $\nu_s/\nu$  factor in the  $E_2$  term of equation 56 accounts for the number of short-range force "bonds" between neighboring particles in a lattice that would be missing if the lattice were expanded to the liquid volume by introduction of randomly placed vacancies.

The proponents of the significant structure theory have found it convenient to relate  $\theta$  to the value  $\theta_D$  of the solid's Debye temperature, taken from low-temperature specific heat measurements. Assuming the solid to be isotropic, homogeneous, and to exhibit no acoustic dispersion, it is possible to show that

$$\theta = 3\theta_D/4 \quad (57)$$

Implicit in assignment of a common  $\theta$  to both anions and cations is the assumption that they execute harmonic motions at the same frequency. More properly,  $\theta$  should be regarded as an average over species.

For ions in gas-like motions, Eyring assumes it appropriate to write a product of diatomic molecule partition functions, since the normal symmetrical salt vapor in equilibrium with the liquid is composed of strongly associated complexes of at least a single anion and cation (51). Polymers larger than the predominant diatomic molecular species, though experimentally detectable, are disregarded. The diatomic molecule partition function is taken to be the usual form (44):

$$Q_{\text{gas}} = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \nu \cdot \frac{8\pi^2 I kT}{h^2} \cdot \frac{\exp[-E_0/kT]}{1 - \exp[-h\nu/kT]} \quad (58)$$

The parameters  $m$ ,  $\nu$ ,  $E_0$ , and  $I$  refer, respectively, to the diatomic molecule mass, vibration frequency (this motion is presumed to be entirely harmonic), dissociation energy including zero-point vibrational energy, and moment of inertia. It should be pointed out that Blomgren (4) considers the alternate partition function formulation for the gas-like particles, wherein these latter are treated as free monatomic ideal gas particles, rather than associated in pairs.

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Having thus obtained results 54 and 58 for the two significant classes of particle motions, the total liquid partition function may immediately be written down, valid for symmetrical salts,

$$Q_N = \frac{1}{[(N(\mathcal{V} - \mathcal{V}_s)/2\mathcal{V})!]^2} [Q_{\text{solid}}]^{N\mathcal{V}_s/\mathcal{V}} \cdot [Q_{\text{gas}}]^{N(\mathcal{V} - \mathcal{V}_s)/2\mathcal{V}} \quad (59)$$

The additional factor  $1/2$  in the exponent of  $Q_{\text{gas}}$  is obviously required by the fact that only half as many gas-like diatomic molecules are present than the number,  $N(\mathcal{V} - \mathcal{V}_s)/\mathcal{V}$ , of ions forming them. The factorial factors in equation 59 must be present to avoid the classical Gibbs paradox (30) associated with requirement that entropy be an extensive property.

In utilizing equation 59, experimental data on the solid state are employed to fix the values of  $E_l$  and  $\theta$ . In addition, the diatomic molecule parameters appearing in  $Q_{\text{gas}}$  are available from spectroscopic investigations. Consequently, only  $n_h$  and  $a/n_h$  remain as adjustables. Among the quantities: melting and boiling temperatures, volume increases, and entropies, at atmospheric pressure, which have not been used to determine these two adjustable parameters, very good prediction of the measured values is obtained in reference 18.

In addition, the approximate molten salt partition function (eq. 59), also allows one to locate a liquid-vapor critical point, by use of the usual conditions on density derivatives of the pressures. Though these apparently have never been observed experimentally, they do not seem entirely inaccessible,\* and will perhaps ultimately provide an interesting test of the significant structures approach.

It is necessary to stress that "derivation" of the approximate liquid-state partition function postulated by the significant structures theory is on an entirely intuitive basis, rather than proceeding from the rigorous expression for  $Q_N$ , equation 29, by an orderly sequence of well-defined mathematical manipulations. As a consequence, it is not very easy to provide *a priori* justification or criticism of the approach. It does seem desirable, though, to point out that a number of questions are raised by this semiempirical theory, which one ultimately would like to examine in the light of a more fundamental analysis:

\* For KBr, for example, Carlson et al. (18) predict  $T_c = 3060^\circ\text{K}$ .,  $p_c = 118.3$  atm.

1. If we could imagine taking an instantaneous photograph of all  $N$  ion positions, knowing simultaneously their momenta, what objective criterion should be used in deciding whether a given particle is gas-like or solid-like? Does this lead to the splitup postulated?

2. It is not at all obvious that the set of particles constituting the quasi-solid structure should behave as particles in the true unmelted solid. In particular, why should the Einstein  $\theta$  be unchanged? Since this quasi-solid framework is pictured as riddled with passageways, it has in effect an extremely large internal "surface area." This latter should modify markedly the properties of such a material, particularly the specific heat, and thereby  $\theta_D$  and  $\theta$ .

3. What is the nature of "strained sites" in the liquid? Why may they all be given a common strain energy?

4. It is not clear what role the fairly complicated dielectric properties of the melt have in this theory. Are their effects on the pressure, for example, entirely implicit in the values ultimately assigned to the two adjustable parameters,  $n_h$  and  $a/n_h$ ?

5. It is hard to imagine that the gas-like particles are sufficiently free to move about in the narrow passageways as the particles of an ideal gas. At best they should be subject to a constant average potential due to the neighboring solid-like particles. A diatomic gas-like molecule should be very seriously hindered in its rotational motion, requiring modification of  $Q_{\text{gas}}$  in equation 58.

In view of the impressive numerical success of the significant structures theory, in the face of these several points of ambiguity, it appears desirable to seek in the future an exhaustive theoretical analysis of the fundamental concepts involved in this method.

#### B. THE "HOLE" THEORY

It is evidently possible to adopt a rather different initial picture of the fused salt medium from that of the significant structures theory, and still predict numerically adequate results for thermodynamic properties. Frenkel (24), Altar (1), and Fürth (25) have been instrumental in developing this alternate view of the general liquid state, and Bockris and Richards (9) have applied the resultant ideas specifically to description of molten electrolytes. This second approximate theory is called the "hole" theory of liquids for reasons that will become clear. There is often semantic confusion of the name of this approach with that of liquid-state cell theories, in which provision

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is made for empty cells. Since just such a theory will be outlined in Section V.3, we shall be careful always to call voids in this third approximate theory "empty cells" or "vacant cells," rather than "holes."

The hole theory is designed to describe spontaneous density fluctuations of molecular extent that occur in liquids, as the constituent particles move about under thermal agitation. In the unmelted crystal, one important such density fluctuation that appears in equilibrium at elevated temperatures is the unoccupied lattice site, or missing particle. On account of the rigid geometrical structure of the crystal, such a small low-density region can be equal in size to only one (or possibly a small integral number) characteristic elementary volume, determined by the crystal structure. Furthermore, motion of these empty regions can proceed only by discrete jumps, produced by a shift of a particle in the crystal into a neighboring unoccupied site. The situation in the liquid is much less restrictive, though, since extra freedom of particle movement attending the melting of the rigid crystal implies not only a continuum of possible sizes and shapes for the low-density regions, or "holes," but movement of these holes may occur by a relatively continuous drift, rather than by discrete jumps.

The specific technique of the hole theory is application of the notions of macroscopic fluid dynamics to the surface and surroundings of the holes. If, first of all, we may extend our knowledge of macroscopic holes—bubbles—in liquids down to the molecular scale of sizes, a hole of a given volume should have as its most stable configuration, a spherical shape. As the liquid particles undergo thermal movements, the resulting motions of the spherical hole will be radial size increase (the "breathing" mode), as well as translation of the hole center through the liquid. It is assumed that the liquid particles (the molten salt ions) outside a given hole comprise an ideal incompressible fluid, whose average motion, for a specified movement of the hole, is given by solution of the hydrodynamic problem of a radially size-varying and translating sphere in this fluid. If the holes are not too numerous, it is permissible to regard them as hydrodynamically independent entities.\*

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\* A really detailed hole theory, beyond what is available at present, would have to account for interference between neighboring holes. Besides being coupled to one another hydrodynamically, a close "collision" could produce a single hole from two, and by microscopic reversibility, the inverse process must be admitted.

These macroscopic concepts allow deduction of a distribution function for a single hole motion and radial size. This distribution,  $f_h(r, p_r, \mathbf{p}_t)$ , may be written as a Boltzmann factor,

$$f_h(r, p_r, \mathbf{p}_t) = b \exp \left\{ -\frac{1}{kT} \left[ w(r) + \frac{p_r^2}{2m_r} + \frac{p_t^2}{2m_t} \right] \right\} \quad (60)$$

involving the reversible work necessary to create a static cavity of radius  $r$ ,  $w(r)$ , plus the kinetic energies associated with radial ( $r$ ) and translatory ( $t$ ) hole motions. These latter, as shown in equation 60, are written in terms of the respective momenta and masses for such motion. The constant  $b$  is determined by the normalization condition:

$$1 = \int_0^\infty dr \int_{-\infty}^{+\infty} dp_r \int_{-\infty}^{+\infty} d^3\mathbf{p}_t f_h(r, p_r, \mathbf{p}_t) \quad (61)$$

The radial momentum  $p_r$  is by definition equal to  $m_r$  times the radial velocity.  $m_r$  is known from classical hydrodynamics (45) to be

$$m_r = 4\pi r^3 \rho_m \quad (62)$$

where  $\rho_m$  is the mass density of the liquid. Similarly,  $\mathbf{p}_t$  is  $m_t$  times the hole center velocity, and the hydrodynamic theory now provides the result (52):

$$m_t = \frac{2}{3} \pi r^3 \rho_m \quad (63)$$

The reversible hole formation work,  $w(r)$ , must be performed both against the pressure applied externally to the liquid and (since a new surface is being created) against the liquid's surface tension,  $\sigma$ . Accordingly, it is traditional in the hole theory to adopt a  $w(r)$  of the form:

$$w(r) = \frac{4\pi r^3}{3} (p - p_0) + 4\pi r^2 \sigma \quad (64)$$

Only the difference between the external pressure,  $p$ , and the liquid's vapor pressure,  $p_0$ , is utilized to account for the possibility of evaporation of liquid particles into the spherical hole, with consequent out-

ward pressure.\* As the liquid is heated up to, and just beyond, the boiling point,  $p_0$  just exceeds  $p$ , so that large holes begin to become probable according to equations 60 and 64; the hole theory identifies these large vapor-filled holes with the usual bubbles observed during the boiling process.

If one is interested only in the distribution of hole sizes,  $F_h(r)$ , irrespective of the radial and translatory momenta, it is only necessary to integrate  $f_h(r, p_r, \mathbf{p}_t)$  over  $p_r$  and  $\mathbf{p}_t$  to obtain (using eq. 60 for  $f_h$ ):

$$\begin{aligned} F_h(r) &= \int_{-\infty}^{+\infty} dp_r \int_{-\infty}^{+\infty} \int d^3\mathbf{p}_t f_h(r, p_r, \mathbf{p}_t) \\ &= Br^6 \exp \left\{ -\frac{w(r)}{kT} \right\} \end{aligned} \quad (65)$$

The constant  $B$  is determined by normalization condition (eq. 61) to be

$$B = \frac{16}{15\sqrt{\pi}} \left( \frac{kT}{4\pi\sigma} \right)^{-7/2} \quad (66)$$

where, for liquids in the neighborhood of the saturation vapor pressure, we have supposed  $p \cong p_0$ , to leave only the surface tension contribution to  $w(r)$  in equation 64. The  $r^6$  factor appearing in  $F_h(r)$  occurs because of the  $r$  dependence of masses  $m_r$  and  $m_t$ .

Now that an explicit distribution function,  $F_h$ , is available for the hole sizes (we shall continue to suppose  $w(r) = 4\pi r^2\sigma$ ), it is a trivial matter to compute the average hole volume,  $\bar{v}$ :

$$\begin{aligned} \bar{v} &= \int_0^{\infty} dr F_h(r) \cdot \frac{4\pi}{3} r^3 \\ &= \frac{32}{15\pi} \left( \frac{kT}{\sigma} \right)^{3/2} \\ &= \frac{32}{15\pi} = 0.6791 \end{aligned} \quad (67)$$

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\* The idea of an included vapor becomes meaningless for holes about the size of the particles. Furthermore, the Gibbs-Kelvin equation (29) indicates that even for larger holes, the included vapor should have lower average density than that of the macroscopic vapor phase in equilibrium with the liquid. These facts have not been properly taken into consideration in the hole theories, to the present.

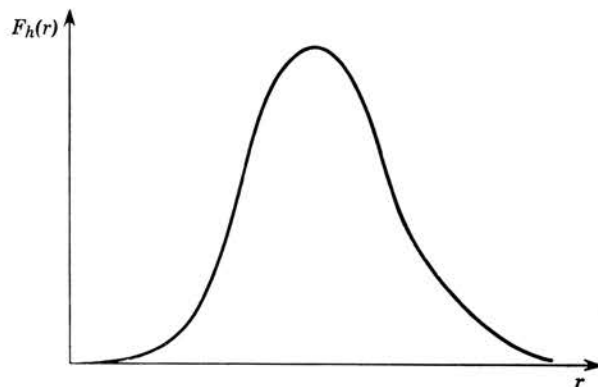


Fig. 7. Schematic plot of the peaked hole size distribution function,  $F_h(r)$ .

By virtue of appearance of  $kT/\sigma$  in this result for  $\bar{v}$ , it is perfectly clear that the surface tension, tending to reduce hole size, is counterbalanced by thermal agitation which, by a sort of radial Brownian motion, acts statistically to increase hole volumes.

In a fashion similar to the  $\bar{v}$  calculation,  $F_h$  may also be used to compute the average surface area of the holes,  $\bar{s}$ . One finds

$$\bar{s} = \frac{7}{2} \left( \frac{kT}{\sigma} \right) \quad (68)$$

If all holes had identical sizes,

$$\begin{aligned} \frac{(\bar{s})^{3/2}}{\bar{v}} &= \frac{(4\pi)^{3/2}}{4/3\pi} \\ &= 10.635 \end{aligned} \quad (69)$$

On the other hand, if the same ratio is formed for the results 67 and 68, the number obtained is 9.643. The small difference reflects the fact that there actually is a finite dispersion in hole sizes. When  $F_h(r)$  is plotted, as schematically in Figure 7, it is seen to be rather peaked about the most probable hole size. This size distribution implies that most holes have volumes close to  $\bar{v}$ .

For KCl at 800°C, in equilibrium with saturated vapor, the surface tension is 96.8 dynes/cm. (5). With this value,  $\bar{v}$  calculated by equation 67 is found to be  $40 \times 10^{-24}$  cm.<sup>3</sup>. If it is supposed that all holes do in fact have the same radius  $r$ , this common radius must

then be 2.1 Å. The holes in this typical alkali halide (similar results are obtained for other salts) therefore are about the right size to accommodate a single ion, and in that sense, are similar to solid-phase empty lattice sites, or vacancies. This small hole size indicates well the considerable extension of macroscopic surface tension and hydrodynamic concepts that is necessary into the molecular domain of the hole theory.

By way of homily, it may be remarked that the hole theory leads to a picture of liquids reminiscent of a portion of Swiss cheese. The holes in this cheese are all about the same size and spherical, and the material (cheese) between the holes is of course more dense than the entire sample considered as a whole. In molten salts, the ions forming the fluid between holes must be rather closely packed, probably at a density comparable to the solid. If this is so, application of pressure to the "Swiss cheese" should affect the holes mainly, since little decrease in volume is possible for material between holes. Similarly, the main contribution to thermal expansion will be due to holes, rather than the constantly dense fluid between them.

If  $\theta_f$  denotes the fraction of the overall liquid volume which is occupied by the dense hole-surrounding fluid, then the compressibility,  $\beta$ , and the thermal expansion,  $\alpha$ , of the liquid will be

$$\begin{aligned}\beta &= \beta_h + \theta_f \beta_f \\ \alpha &= \alpha_h + \theta_f \alpha_f\end{aligned}\tag{70}$$

The subscripts  $h$  and  $f$  on  $\alpha$  and  $\beta$  denote, respectively, the total hole, and pure surrounding fluid parameters.

To evaluate the hole contributions to liquid compressibility and thermal expansion, it is necessary to estimate the number of holes present,  $N_h$ . The nearest neighbor distance observed in liquids by x-ray scattering, which must be characteristic of particle stacking in the hole-surrounding fluid, changes little on melting; the hole theory concludes then, that the melting volume increase  $\Delta\mathcal{V}_m$  must primarily be due to volume consumed by holes introduced into the system upon melting. Since it has been found that most holes have volumes very near  $\bar{v}$ , it is reasonable to determine  $N_h$  by

$$\Delta\mathcal{V}_m = N_h \bar{v}\tag{71}$$


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At temperatures well above the melting point,  $N_h$  may still be obtained from relation 71, but  $\Delta\mathcal{U}_m$  must be interpreted as the difference between the measured liquid volume and the extrapolated volume of an hypothetical superheated crystalline solid.

With this more complete picture as to the number of holes, in addition to their size distribution, the parameter  $\theta$  of equation 70 must therefore be

$$\theta_f = \frac{\mathcal{V} - \Delta\mathcal{U}_m}{\mathcal{V}} \quad (72)$$

Also, since near-neighbor pairs in the hole-surrounding fluid are arranged much as in the solid, it is supposed that  $\beta_f$  and  $\alpha_f$  are adequately approximated by the solid-phase values extrapolated to the temperature of interest.

Because both  $N_h$  and  $\bar{v}$  are generally temperature and pressure dependent,

$$\begin{aligned} \beta_h &= -\frac{1}{\mathcal{V}} \left( \frac{\partial(N_h\bar{v})}{\partial p} \right)_T \\ &= -\frac{N_h}{\mathcal{V}} \left( \frac{\partial\bar{v}}{\partial p} \right)_T - \frac{\bar{v}}{\mathcal{V}} \left( \frac{\partial N_h}{\partial p} \right)_T \end{aligned} \quad (73)$$

and

$$\begin{aligned} \alpha_h &= \frac{1}{\mathcal{V}} \left( \frac{\partial(N_h\bar{v})}{\partial T} \right)_p \\ &= \frac{N_h}{\mathcal{V}} \left( \frac{\partial\bar{v}}{\partial T} \right)_p + \frac{\bar{v}}{\mathcal{V}} \left( \frac{\partial N_h}{\partial T} \right)_p \end{aligned} \quad (74)$$

In application of the hole theory to molten salts, it is assumed that all, or nearly all, holes are introduced into the liquid as the solid melts, and that temperature and pressure variations in the liquid cause negligible changes in  $N_h$ . Consequently the last term in each of equations 73 and 74 are dropped.

The remaining partial derivatives occurring in  $\beta_h$  and  $\alpha_h$  may be evaluated from the definition (eq. 67) of  $\bar{v}$ . Using the integrated form of equation 67,

$$\alpha_h = \frac{3N_h\bar{v}}{2kT} \quad (75)$$

When the more elaborate pressure-dependent form for  $w(r)$ , equation 64, is inserted in equation 67,  $\beta_h$  is subsequently found to be

$$\beta_h = \frac{N_h}{kT} [\overline{v^2} - (\bar{v})^2] \quad (76)$$

$\overline{v^2}$  is the mean *square* hole volume. Therefore,  $\beta_h$  is directly related to the dispersion in hole volumes. If the former assumption that all holes have precisely the same size were entirely correct, this expression for  $\beta_h$  would vanish identically. But from the actual distribution  $F_h(r)$ , now without the pressure terms in  $w(r)$ , an elementary computation yields

$$\beta_h = 0.4713 \frac{N_h(\bar{v})^2}{kT} \quad (77)$$

Using the concepts and deductions of the simplified hole theory outlined here, Bockris and Richards (9) have computed values of  $\beta$  and  $\alpha$  for a large number of salts.\* The results are in fair agreement with observed values, being generally within 20%.

As in the previously sketched significant structures theory, the hole theory has not as yet been provided with a systematic derivation by clear-cut approximation procedures from the exact liquid partition function. The most obvious omission in available expositions of the hole theory is precise definition of "holes" in terms of instantaneous particle positions.

It is interesting that no explicit properties of the individual molecules or ions forming the liquid of interest appear in the hole theory formalism. Only macroscopic observables—melting volume increases and surface tensions—are used. Specifically, the hole theory contains no indication on an *a priori* basis, that electrostatic forces between ions of a fused salt should cause characteristic behavior for these liquids, as contrasted with non-electrolytes.

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\* Bockris and Richards actually have employed a constant value  $\theta_f = 0.37$ , due to Fürth (25), somewhat different from that quoted in equation 72; this magnitude is difficult to reconcile with the apparent model of liquids implied by the hole theory. If most of the molten salts' volume changes are attributable to variations in  $\bar{v}$ , computed  $\alpha$  and  $\beta$  would be relatively insensitive to the value chosen for  $\theta_f$ . In addition, the numerical constant 0.4713 used in expression 77 for  $\beta_h$  differs from Fürth's multiplicative constant ( $9/14 = 0.6492$ ) by about 27%.