Compressibility of Simple Fused Salts

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It is pointed out that the isothermal compressibility of monatomic molten salts should nearly equal that for a hypothetical fluid of uncharged ion cores at the same over-all particle density as the salt. The validity of this relation is equivalent to verification of conjectures concerning the number-average correlation function for ion pairs in the melt. When the ion core forces are treated as those acting between rigid spheres, it is readily possible to predict the distance of closest approach for an anion-cation pair from experimentally determined compressibilities. The corresponding distances obtained in this manner for a series of molten halides are consistent with known ion sizes, and furthermore exhibit the proper homologous series trends.

I. THEORETICAL CONSIDERATIONS

IN a recent analysis of ionic distributions in fused salts,[1] it was shown that an order-disorder treatment of these "binary mixtures" of anionic and cationic particles could formally reduce the problem of computing the canonical partition function for these substances to that for a fluid (at the same temperature and over-all number density as the salt) all of whose particles are identical. The effective potential energy acting in this equivalent fluid was found to be equal (in the case of identical ion core forces for all ion pairs) to the short-range interaction of the original ion cores, supplemented by temperature-dependent corrections arising from nonrandom mixing of ions in the melt. These latter contributions are primarily attractive, and are of considerably shorter range than the original Coulomb interactions in the salt.

Fused salts, at or not too far above their normal melting points, are typical dense liquids in the sense that the spherical constituent particles are rather closely packed together. As a consequence, there is relatively little freedom for rearrangement of the entire set of particle positions, which fact gives rise to small values of the isothermal compressibility. On the other hand, for a given set of particle positions, the Coulomb interactions between ions appear to "sort" the ions in the melt into a pseudo-crystalline array rather like the regular solid.[1] Thus, any given ion on the average is surrounded by spherical shells of electrostatic change of alternating sign, just as in the unmelted crystal, where successive shells of neighbors differ in charge sign. The effect of this sorting is, naturally, to lower the liquid's energy by a large amount, comparable in magnitude to the solid phase Madelung energy.

Although the powerful Coulomb forces produce a position discrimination between ions of different charge sign, if one were to fail to distinguish between anions and cations in a salt whose impenetrable ion cores were virtually alike (equal anion and cation size), the rela-

tively few configurations available to these closely packed cores seems to imply that the over-all distribution of identical cores is little affected by the presence of ionic charge.[2] If this conjecture is correct, then the number-average pair correlation function, $g_m(r)$, in the dense fused salt should virtually equal that for a fluid composed of only the uncharged cores.[3] Thus, the temperature-dependent portion of the effective interaction for the "equivalent fluid" appears to have little effect on the total particle pair correlation function.

To be specific, in a salt whose various ions are present in number densities $\rho_1, \cdots, \rho_\nu$, $g_m(r)$ is related to the individual pair correlation functions $g_{\alpha\beta}{}^{(2)}(r)$ by

$$g_m(r) = \left[\sum_{\alpha,\beta=1}^{\nu} \rho_\alpha \rho_\beta \right]^{-1} \sum_{\alpha,\beta=1}^{\nu} \rho_\alpha \rho_\beta g_{\alpha\beta}{}^{(2)}(r). \tag{1}$$

Of course, the set of densities ρ_α is constrained to satisfy the electroneutrality condition:

$$\sum_{\alpha=1}^{\nu} (z_\alpha e)\rho_\alpha = 0, \tag{2}$$

where the electrostatic charge on an α-type ion is some small integer z_α times the protonic charge e. It is our claim that $g_m(r)$ is almost entirely determined by the short-range ion core forces alone, at least for salts with equal ion sizes.

The strong tendency to "sort" the ions in the melt according to charge implies that the powerful Coulomb repulsion between like ions is effective in preventing close contact except between anion-cation pairs. As a result, for simple pure salts containing single anionic and cationic species, the only short-range core forces that come into play are those acting between pairs of unlike ions.[1] Therefore, the details of ion core short-range forces for pairs of like ions are irrelevant in deter-

[1] F. H. Stillinger, J. G. Kirkwood, and P. J. Wojtowicz, J. Chem. Phys. **32,** 1837 (1960).

[2] It is assumed here that sufficiently powerful external wall forces are present to maintain the over-all particle density fixed, whether or not electrostatic charges are present.

[3] For a comprehensive discussion of molecular distribution functions (specifically, the pair correlation function), see: T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 6.

mining the thermodynamic properties of the fused salt. In a statistical mechanical model of molten salts, therefore, it appears permissible to assume that all short-range ion core forces are the same, and equal specifically to those acting between unlike ions in the salt of interest. In this sense, it is possible to relate salts with ion radius ratios deviating somewhat from unity to a model salt with equal-sized ions.

If this second conjecture is valid, salts with unequal ion sizes also should exhibit mean pair correlation functions determined only by core interactions. In this case, however, $g_m(r)$ refers to the hypothetical nonelectrolytic fluid whose particles interact according to precisely the anion-cation short-range potential. This more general case of unequal ion size thus effectively reduces to the more convenient special case of equal sizes.

The possible use of only the anion-cation core interaction has recently been exploited by Reiss, Mayer, and Katz in the development of a corresponding-states theory of molten salts.[4] The apparent success of their treatment may be regarded as an independent confirmation of the present hypotheses about fused salt structure. Although Reiss, Mayer, and Katz find it necessary to specify a complete interaction potential for the ionic assembly, such considerations are unnecessary in the present context. In particular, there may be difficulty in defining local dielectric constants to account completely for polarization interactions in the liquid.

The replacement procedures for like ion pair core forces by those for unlike pairs is justified, unless the original radius ratio (anion to cation) is very large. In the latter case, large anions could easily be in contact with one another, and the very much smaller cations would simply occupy the interstices between the anions. Therefore, in salts such as LiI, where the ratio is about 3.5, one should anticipate deviation from the common ion size model predictions.

In the case of fluids consisting of a single type of particle, it is known that the isothermal compressibility,

$$\kappa = -1/V(\partial V/\partial p)_T \tag{3}$$

($V =$ volume, $p =$ pressure, $T =$ absolute temperature), is related to an integral of $g^{(2)}(r)$, the pair correlation function in that fluid[5]:

$$\rho k T \kappa = 1 + \rho \int_0^\infty [g^{(2)}(r) - 1] \cdot 4\pi r^2 dr. \tag{4}$$

ρ denotes the number density of particles in this fluid, and k is Boltzmann's constant. If our assumptions about the microscopic structure of dense fused salts are valid, then the formal equivalence of the statistical thermodynamics of the salt to that of a single component fluid implies that the salt isothermal compressibility also should be given by relation (4), but where

$g^{(2)}(r)$ is to be replaced by $g_m(r)$. Furthermore, this latter mean correlation function should for all intensive purposes be equal to the pair correlation function for a fluid of uncharged ion cores, at the same temperature and over-all density as the fused salt, but with particle diameters all equal to the distance of closest approach between a pair of unlike ions.

Although, in the strict sense, ion core interactions are presumably well-defined functions for all pair separations r, the fact of very strong repulsion relative to kT even at molten salt temperatures, when r is less than the "contact" value, makes it convenient to replace the actual core potential by one appropriate to rigid spheres with some collision diameter, a. Under this circumstance, κ for the molten salt could be computed by Eq. (4) from the known correlation function for rigid spheres.[6]

Reiss, Frisch, and Lebowitz[7] have developed a statistical mechanical theory of the rigid sphere fluid which not only yields good agreement with known values of the virial coefficients for this system, but also quantitatively reproduces the Monte Carlo results for the dense fluid equation of state.[8] Their results may be displayed in the form:

$$p = \frac{6kT}{\pi a^3} \frac{y(1+y+y^2)}{(1-y)^3}.$$

$$y = \pi \rho a^3/6. \tag{5}$$

Differentiation of this equation of state with respect to V leads to:

$$\rho k T \kappa = (1-y)^4/(1+2y)^2. \tag{6}$$

If Eq. (4) is compared with this expression, it becomes clearly unnecessary to integrate the entire hard sphere pair correlation function at each density, since[9]

$$\int_0^\infty (r/a)^2 [g^{(2)}(r/a) - 1] d(r/a) = \frac{(y-4)(y^2+2)}{24(1+2y)^2}. \tag{7}$$

If, for a given fused salt observed at temperature T, measured values of the total ion number density and the isothermal compressibility are respectively substituted for ρ and κ in relation (6), it is subsequently possible to assign a unique value of y to this liquid. Furthermore, this deduced value of y, along with the already used value ρ of the total ion number density, allows the corresponding distance of closest anion-cation approach

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[4] H. Reiss, S. W. Mayer, and J. Katz (to be published).
[5] See reference 3, p. 236.

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[6] J. G. Kirkwood, E. K. Maun, and B. J. Alder, J. Chem. Phys. **18**, 1040 (1950).
[7] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).
[8] W. W. Wood and J. D. Jacobsen, J. Chem. Phys. **27**, 1207 (1957).
[9] Assuming that the Reiss, Frisch, and Lebowitz equation of state (5) is substantially exact in the fluid range of densities for the rigid sphere system, Eq. (7) may be regarded as an interesting test of the accuracy of computed pair correlation functions for this system.

to be obtained from y's definition:

$$a = (6y/\pi\rho)^{\frac{1}{3}}. \qquad (8)$$

If our assumptions are *not* justified, that

(a) the mean correlation function $g_m(r)$ in a dense fused salt with equal ion sizes is virtually equal to that for the fluid of uncharged cores,

(b) salts with ion size ratios differing moderately from unity are equivalent to salts with ratio unity, but the same anion-cation distance of closest approach, then the discrepancy should affect the values of a computed from Eqs. (6) and (8). It is the purpose of this article to compare values of a obtained in this manner with known crystal radii for the ions involved, with a view toward providing at least partial verification of (a) and (b).

II. NUMERICAL RESULTS AND DISCUSSION

The isothermal compressibilities for a series of molten halides are available from the sound velocity measurements of Bockris and Richards.[10] The corresponding densities for alkali halides have been measured by Yaffe and Van Artsdalen.[11] In the case of the one unsymmetrical electrolyte considered, $CdCl_2$, we have utilized the density measurements of Boardman, Dorman, and Heymann.[12]

Table I displays the anion-cation distances of closest approach computed from Eqs. (6) and (8), along with the corresponding sum of crystal radii.[13] In all cases, general agreement is observed. The computed distances deviate on the low side from the crystal values, undoubtedly because the latter correspond roughly to the minimum of the anion-cation potential curve rather than to the rapidly rising repulsive portion of this curve, which, at somewhat smaller separations, more nearly corresponds to the rigid sphere behavior postulated. This point of view is borne out by the fact that increasing temperatures yield decreased effective collision diameters; the more energetic thermally-produced collisions give rise to greater degrees of core interpenetration, since of course the ion cores are not completely rigid.

What is perhaps most significant is the fact that computed distances for each homologous series (e.g.,

[10] J. O'M. Bockris and N. E. Richards, Proc. Roy. Soc. (London) **241**, 44 (1957).

[11] I. S. Yaffe and E. R. Van Artsdalen, J. Phys. Chem. **60**, 1125 (1956).

[12] N. K. Boardman, F. H. Dorman, and E. Heymann, J. Phys. Chem. **53**, 375 (1949).

[13] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., p. 514.

TABLE I. Values of the anion-cation collision diameter computed from the fused salt isothermal compressibilities. The corresponding sums of Pauling ionic crystal radii appear in parentheses. All distances are Angstrom units.

T °C		600	700	800	900	1000
LiCl	(2.41)		2.31	2.26	2.20	2.14
NaCl	(2.76)			2.47	2.41	2.34
KCl	(3.14)			2.70	2.63	2.55
CsCl	(3.50)		3.01	2.93	2.84	2.74
LiBr	(2.55)	2.55	2.49	2.43	2.38	2.31
NaBr	(2.90)			2.63	2.58	2.51
KBr	(3.28)			2.85	2.78	2.70
CsBr	(3.64)		3.06	2.98	2.88	2.75
NaI	(3.11)		2.88	2.82	2.74	2.66
KI	(3.28)		3.09	3.01	2.93	2.82
CdCl₂	(2.78)	2.50	2.45	2.39		

the chlorides of lithium, sodium, potassium, and cesium) retain the correct increasing order as one travels down the periodic table. This increase follows increase of either cation or anion atomic number in a given series.

In addition, the temperature variation of the effective collision diameter a appears to be slightly less for smaller ions. This is consistent with the fact that the smaller outermost (valence) orbital electrons in ions of low atomic number are held more stiffly in position than the more extended orbital electrons for large ions. Accordingly, it is harder to displace electrons in the former case in an ion pair collision, and so the smaller ions act as more nearly rigid spherical particles.

In the case of LiBr (radius ratio greater than 3), and somewhat less obviously in the case of LiCl (ratio about 3), there seems to be a tendency among the computed distances to deviate positively from the percentagewise decrease, observed in the case of the other salts, of computed a below the crystal distance. This deviation probably marks the onset of nonnegligible anion-anion contacts in the melt, and therefore seems to indicate breakdown of possible application of a single-ion-size model to these melts.

In conclusion, consequently, it appears that hypotheses (a) and (b) concerning the microscopic structure of melts are consistent with the experimental compressibility data, especially in view of the several characteristics of ion core forces which, as indicated by the numerical calculations, are preserved under the scheme outlined in the preceding section.