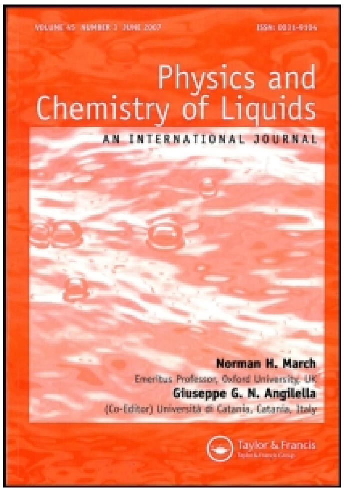

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Theories of the Thermodynamic Properties of Pure Molten Salts

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The analytical theories may be classified into (a) the older, semi-empirical theories, in which the approximations are physically motivated and rather unsystematic; typical of these are the so-called Significant Structures and Hole theories; (b) the newer theories, which we will, rather arbitrarily, refer to as the fundamental theories; here the approximations are of a more mathematical character and more systematically introduced; the perturbation and variational theories exemplify this approach. In addition, there are the Corresponding States methods, which occupy an intermediate position, in that, while having some fundamental justification, they are generally applied in an empirical manner.

It is instructive to compare the state of the theoretical art for molten salts with that for simple, non-ionic liquids. The newer theories have proved so successful for the latter that it is now possible to calculate their thermodynamic and structural properties for any density and temperature, using only very modest computational facilities, once the interatomic potential is specified.[12–14] In this sense, the semi-empirical theories are now obsolete for these liquids. As we shall show, this is not yet the case for molten salts, where the older theories still have their uses.

In the first part of this review, we describe two theories which typify the semi-empirical approach: the Significant Structures and Hole theories. This is followed by a summary of Corresponding States methods. We then go on to discuss the newer, fundamental theories. We attempt to show what success they have so far achieved and what obstacles remain to be overcome before our understanding of molten salts is on a par with that of simple liquids.

2 STATISTICAL MECHANICS

The formal statistical mechanics underlying the calculation of thermodynamic properties is quite clear. If we have a system consisting of N_α particles of species $\alpha(\alpha = 1, 2, \ldots, \nu)$ contained in volume V at temperature T, then the Helmholtz free energy $F(V, T)$ of the system is given by

$$F(V, T) = -kT \ln Q \tag{1}$$

$$Q = \left(\prod_{\alpha=1}^{\nu} N_\alpha! \Lambda_\alpha^{3N_\alpha}\right)^{-1} Z, \tag{2}$$

$$Z \doteq \int \prod_{i\alpha} d\mathbf{r}_{i\alpha} \exp(-\beta U), \tag{3}$$

where $\mathbf{r}_{i\alpha}$ is the position of the ith particle of species α, U is the total potential energy of the system, which depends on the set of positions $\{\mathbf{r}_{i\alpha}\}$ and Λ_α is the thermal wavelength of species α; the integrations in Eq. (3) extend over the volume V. Once the free energy is known, all the other thermodynamic functions follow by the usual relations.

There are two problems in the practical application of these equations:

a) the construction of a realistic representation of the potential U and

b) the evaluation of the multi-dimensional integral in equation (3).

For the alkali halides at least, the first problem is to a large extent solved.[11] The total potential energy may be adequately represented by a sum of pair potentials:

$$U = \frac{1}{2} \sum_{\alpha,\beta} \sum_{i,j}{}' \phi_{\alpha\beta}(|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}|), \tag{4}$$

where the prime on the sum indicates that $i \neq j$ if $\alpha = \beta$. The interionic potentials $\phi_{\alpha\beta}$ are, to a good approximation, given by the sum of coulomb, exponential repulsion and dispersion terms:

$$\phi_{\alpha\beta}(r) = \frac{z_\alpha z_\beta}{r} + B_{\alpha\beta} e^{-r/\rho} - \frac{C_{\alpha\beta}}{r^6} \tag{5}$$

where z_α is the charge on ions of species α. Methods of determining the coefficients $B_{\alpha\beta}$ and $C_{\alpha\beta}$ are discussed in Ref. 11. This representation may be refined by the addition of ionic polarizability and higher-order dispersion terms, but for the alkali halides at least, these appear to have only a small effect on the thermodynamic properties.[15] For salts which are appreciably covalent, for example the halides of group IB, the above representation will, of course, be less adequate.[16]

Even if the potential is known, there remains the problem of calculating the integral in Eq. (3), and this has been the main stumbling block to the calculation of thermodynamic properties for molten salts. We now turn to the methods which have been used to tackle, or circumvent, this problem.

3 SEMI-EMPIRICAL THEORIES

3.1 Significant Structures

The Significant Structures theory of liquids is based on physical ideas originally proposed by Eyring[17] to describe the phenomena of melting and viscosity. The full mathematical formulation of these ideas was given much later by Eyring and his coworkers[18–21] and has since been extensively applied and discussed.[22–23] It should be mentioned that serious reservations have been expressed about the fundamental validity of the theory.[28] However, it does turn out to give qualitatively correct predictions.

The basic idea is that the configurations in which an atom or ion finds itself in a liquid are intermediate between those typical of a solid and those typical of a gas. This means that an atom will spend part of its time vibrating in a cage of surrounding atoms and the remainder translating freely as it would in the gas phase. The weights which are assigned to these two kinds of configurations in the partition function are assumed to be determined only by the density of the liquid and to be linear in the ratio between this density and the density of the solid at the triple point.

For a uni-univalent molten salt, such as an alkali halide, these ideas can be formulated as follows.[20,23,26] Consider a system containing N ions of each species at temperature T contained in volume V. Let V_s be the volume of the solid at the triple point. Then the partition function is approximated by

$$Z = z_s^{NV_s/V} z_g^{N(V-V_s)/V}, \tag{6}$$

where z_s and z_g are the partition functions for a molecular unit in the solid and the gas respectively. The partition function for the gas phase z_g is that appropriate to a bound ion pair; it may be written as the usual product of translational, vibrational and rotational factors. (Dissociation of such pairs only occurs at such low densities or such high temperatures that it is of no interest in the present context; association into more complex clusters does, however, occur[29] and may be included in z_g if necessary.[22])

As an approximation to the solid partition function z_s one takes the Einstein model of independent oscillators:

$$z_s = e^{-\beta E_s}\left(\frac{kT}{h\nu_s}\right)^6, \tag{7}$$

where E_s is the binding energy per molecule and ν_s is a mean vibrational frequency in the solid. Eyring argues that this formula needs to be modified in two ways when used in the liquid-state partition function. Firstly, an ion in the liquid, though bound in a solid-like configuration, may be capable of occupying a number n_h of sites which are distinct from the most stable one. These additional sites are assigned the energy—$a'E_s/n_h$, a' being an adjustable parameter; then the formula (7) needs to be multiplied by the factor $(1 + n_h \exp(\beta a' E_s/n_h))$. The number n_h is assumed to depend on the density as follows:

$$n_h = \frac{n(V - V_s)}{V}, \tag{8}$$

where n is a further adjustable parameter. Secondly, in an ionic substance, the dominant contribution to the cohesive energy comes from the coulomb potential, which is of long range. This suggests that E_s should be allowed to depend on the density.[20] A convenient procedure for dealing with this is to replace E_s by $E_s(V/V_s)^\gamma$, where γ is a third parameter. With these modifications, the solid partition function takes the form

$$z_s = \exp\left(-\beta E_s\left(\frac{V}{V_s}\right)^\gamma\right)\left(1 + n_h \exp\left(\frac{\beta a' E_s}{n_h}\right)\right)\left(\frac{kT}{h\nu_s}\right)^6. \qquad (9)$$

On inserting the resulting equations for z_g and z_s into equation (6) and the latter into Eqs. (1) and (2), we obtain an expression for the free energy, from which all other functions can be found.

The theory contains three empirical parameters, n, a' and γ in addition to the binding energy E_s, the mean Einstein frequency ν_s and the gas-phase molecular properties. For the alkali halides and many other substances, the gas-phase parameters can be obtained from spectroscopic measurements; the parameters E_s and ν_s are most conveniently obtained from measurements of the vapour-phase pressure over the solid. The empirical parameters n, a' and γ must be determined by fitting to experimental thermodynamic data. Clearly there are many ways of doing this. Since the Significant Structures theory claims to describe the thermodynamics of melting as well as that of the liquid itself, a possible and often-used procedure is to employ the melting temperature and the volume and entropy changes on melting as the three required pieces of empirical data.

Several studies of the molten alkali halides have been made using Significant Structures theory.[20,22,23,26] It should be borne in mind that experimental data for the liquid are available for most of these salts only up to the normal boiling point,[30–32] so that a full test of the theory is not possible at present. The internal energy and density of the liquid at the melting point are fixed by the thermodynamic input data and are therefore correct by construction. However, the specific heat c_v, the expansion coefficient α and the isothermal compressibility β_T are genuine predictions, and may be used to assess the theory.

In Table I we show theoretical results for these quantities for a selection of alkali halides together with experimental results. The specific heat c_v is well predicted and is in error typically by only 10%; the theory also correctly reproduces the decrease of c_v with increasing temperature.[23,26] The expansion coefficient is in reasonable ($\sim$30%) agreement with experiment.[22,23,26] The compressibility is rather poorly described, being in error typically by a factor of two;[22,23,26] however, it shows the expected increase with temperature.

In spite of its obvious crudity, then, the Significant Structures theory gives a qualitative account of the thermodynamics of pure alkali halides. This provides some justification for its use as an extrapolative technique[26,27] in the theory of molten salts.

TABLE I

Comparison of Significant Structures theory with experiment for molten alkali halides at the melting point for specific heat at constant volume c_v, expansion coefficient α and isothermal compressibility β_T. Theoretical results from Ref. 26.

Salt		NaBr	KCl	KBr	KI
Melting Temperature (K)[34]		1020	1043	1007	954
C_v(cal mole^{-1}K^{-1})	Theory	11.5	11.7	11.8	11.8
	Expt.[33]	12.0	11.2	11.6	10.1
$\alpha(10^{-4}K^{-1})$	Theory	6.12	3.66	3.81	4.53
	Expt.[34]	3.50	3.84	3.91	3.89
$\beta_T(10^{-12}cm^2dyn^{-1})$	Theory	27.4	15.3	17.5	23.5
	Expt.[33]	31.6	36.2	39.8	46.7

3.2 Hole theory

The concepts of Hole theory, like those of Significant Structures theory, are of some antiquity,[35–38] but again were not applied to molten salts until the late fifties.[33] The idea is that the structure of the liquid can be represented as a uniform medium containing voids or holes. The thermodynamic properties of the uniform medium are taken to be the same as those of the solid, extrapolated to the state of interest. The holes are treated as independent statistical-mechanical entities; the configuration of a hole is specified by its position and radius. The hole radius R is subject to a Boltzmann distribution $f(R)$:

$$f(R) \sim e^{-\beta w(R)}, \tag{10}$$

the free energy $w(R)$ being written down as if the hole were a macroscopic void:

$$w(R) = \tfrac{4}{3}\pi R^3(p - p_0) + 4\pi R^2\sigma, \tag{11}$$

where p is the external pressure, p_0 the vapour pressure and σ the surface tension. On the basis of these assumptions, a partition function and hence a free energy of the liquid can be constructed.

It is clear that the Hole theory is in principle much more limited in scope than the Significant Structures theory, since it makes physical sense only in the dense liquid region; in particular, it has nothing to say about the vapour region.

The theory has been successfully applied to calculate the compressibility and expansion coefficient as a function of temperature for many of the alkali halides and nitrates[33] in the neighbourhood of the triple point. The agreement with experiment is surprisingly good: the average discrepancies are

~20% for both the compressibility and the expansion coefficient. The temperature dependence of the two quantities is also well reproduced. For a more detailed discussion of the Hole theory as applied to molten salts, reference[33] may be consulted.

4 CORRESPONDING STATES THEORIES

The semi-empirical theories described above propose physical solutions to the problem of evaluating the partition-function integral. Corresponding States theory has the more modest objective of correlating the thermodynamic properties of liquids within a certain class. As is well known,[39–41] this theory says that the equation of state is the same, apart from an appropriate scaling, for all members of the class. This implies, for example, that the so-called compressibility factor $Z = PV/RT$ is a universal function of reduced independent variables, e.g. volume and temperature:

$$Z = Z(V_r, T_r); \tag{12}$$

the reduced quantities V_r and T_r are given in terms of the actual volume and temperature V and T by

$$V_r = \frac{V}{V_0}$$

$$T_r = \frac{T}{T_0},$$

where the reference volume and temperature V_0 and T_0, often, but not necessarily, chosen to be those appropriate to the critical point, are different for each liquid in the class.

As was first pointed out by Pitzer,[42] the Corresponding States theory follows from a dimensional analysis of the partition function, Eqs. (1)–(3), if the interparticle potentials for all liquids in the class are related by simple scaling of energy and length.

In spite of this requirement on the similarity of the potentials, the theory is sometimes used to predict the properties of molten salts on the basis of a comparison with a class of completely unrelated non-ionic materials.[43]

The theory has been more appropriately applied to correlate properties within the class of molten alkali halides.[4,5,44–46] Even in this case it might appear implausible to assume that the inerionic potentials are similar in

TABLE II

Test of Corresponding States theory for molten alkali halides at the melting point. According to the theory, the dimensionless quantity τ_m should be the same for all the alkali halides. Adapted from Refs. 5 and 44.

Salt	Melting point T_m(K)	σ (Angstroms)	$\tau_m = \sigma k T_m / z^2 \times 10^2$
LiF	1121	2.01	1.35
LiCl	887	2.57	1.36
LiBr	823	2.75	1.35
LiI	718	3.02	1.30
NaF	1265	2.31	1.75
NaCl	1074	2.81	1.81
NaBr	1023	2.98	1.82
NaI	933	3.23	1.80
KF	1129	2.67	1.80
KCl	1045	3.14	1.96
KBr	1013	3.29	1.99
KI	958	3.53	2.02
RbF	1048	2.82	1.77
RbCl	988	3.29	1.95
RbBr	953	3.43	1.96
RbI	913	3.66	2.00
CsF	955	3.01	1.72
CsCl	918	3.47	1.91
CsBr	909	3.62	1.97
CsI	894	3.83	2.05

the required sense. After all, for any given salt there are three interionic potentials (cation–cation, cation–anion and anion–anion), which contain at least two different lengths (the ionic radii). A single length scaling is therefore insufficient to bring into coincidence the potentials for two different salts. However, as Reiss *et al.*[44] have pointed out, the dominant part of the potential, apart from the coulomb contribution, is the repulsion between unlike ions; the non-coulombic repulsion between like ions plays a very minor role, since the coulombic repulsion ensures that these are well separated. This idea has been amply confirmed by recent computer-simulation calculations.[10,15] Reiss *et al.*[44] go on to suggest that the true potential may be replaced by the sum of the coulomb potential and a hard-sphere repulsion between unlike ions. The only parameters entering the three interionic potentials are now the hard sphere diameter σ and the energy z^2/σ, z being the ionic charge; the Corresponding States theory then follows rigorously.

In fact, the assumption of a hard sphere repulsion is unnecessarily restrictive.[4,45] A more general assumption, which still permits the derivation of Corresponding States theory, is that the repulsion between unlike ions is proportional to an inverse power of the separation. The interionic potentials may then be written

$$\begin{aligned}\phi_{++}(r) &= \phi_{--}(r) = \frac{z^2}{r} \\ \phi_{+-}(r) &= -\frac{z^2}{r} + \frac{\alpha}{r^n}\end{aligned} \tag{15}$$

where α is a constant which will vary from salt to salt, and the exponent n is constant within the class. If we now choose a length σ such that $\alpha/z^2 = \sigma^{n-1}$ and denote z^2/σ by ϕ_0, the interionic potentials may be rewritten

$$\begin{aligned}\phi_{++}(r) &= \phi_{--}(r) = \frac{\phi_0\sigma}{r} \\ \phi_{+-}(r) &= \phi_0\left(-\frac{\sigma}{r} + \left(\frac{\sigma}{r}\right)^n\right).\end{aligned} \tag{16}$$

The potentials for all salts in the class are now identical apart from the length scale σ and the energy scale ϕ_0. If Eq. (16) is substituted into Eqs. (1)–(3), it is readily shown that the equation of state may be cast in the form

$$\pi = \pi(\theta, \tau), \tag{17}$$

where the reduced pressure π, temperature τ and volume θ are given by

$$\pi = \frac{\sigma^4 P}{z^2} \tag{18}$$

$$\tau = \frac{\sigma k T}{z^2} \tag{19}$$

$$\theta = \frac{V}{N\sigma^3}. \tag{20}$$

Reiss *et al.* show that the Corresponding States relations (17)–(20) provide a good correlation of the melting temperatures of the alkali halides. If the foregoing theory is correct, the value τ_m of τ at the melting point ought to be the same for all the alkali halides. If σ is identified with the nearest neighbour distance in the solid, this expectation is very well satisfied, except for the lithium salts, which are all deviant. It has also been shown that the relations provide a good correlation for the enthalpy of vaporization and the vapour pressure of the liquid alkali halides,[4,5,44] the lithium salts being again exceptional. The discrepant behaviour of the lithium halides is usually[4,5,44] attributed to the small size of the lithium ion: because of this, the cations will be ineffective in keeping the anions apart and the short-range repulsions between the latter will be operative—an effect which has been intentionally neglected. It seems unlikely that this is the whole explanation, since the ratio of the cation to anion ionic radii in LiF is much the same as that of the anion to cation radii in CsF.

It is clearly not necessary to use melting-point data in establishing the scaling; such a choice may, indeed, be unwise, since it assumes in effect that the same corresponding States relations are valid from the solid and for the liquid. Young and O'Connell[46] have used as reference the volume and temperature of the saturated liquid at which $(d \ln V/d \ln T)_P = 0.4$, which falls in the liquid range for all the alkali halides. They show that there is an excellent Corresponding States correlation for the liquid density as a function of temperature; however Adams and McDonald[45] point out that the results they present demonstrate nothing more than the linear dependence of density on temperature, an empirical relation which is well known to be valid for a much wider class of liquids than the molten salts.[39] A more extensive and systematic study of Corresponding States for molten salts, not based on melting-point data would be of some interest, as would a clarification of the reasons for the deviation of the lithium halides from the otherwise coherent alkali halide scheme.

5 FUNDAMENTAL THEORIES

As far as the simple liquids are concerned, the semi-empirical theories of the kind we have just described are now entirely obsolete. The theories which have displaced them provide a systematic and accurate means of calculating the thermodynamic properties in terms of a given interatomic potential. The attainment of this desirable state of affairs for molten salts is clearly an important theoretical goal. In this section we attempt to summarise the progress so far achieved in this direction.

5.1 Approximations for simple liquids

In order to do this, we must first sketch the methods which have proved so successful for simple liquids. Several excellent reviews of these are available,[12–14,47] so we intend to be brief. All the fundamental theories proceed by relating the properties of the required system to those of a so-called reference system, whose thermodynamic properties and radial distribution functions are supposed to be known. For simple liquids, the reference system is always chosen to be the hard sphere system. This choice is motivated by several important considerations:

a) the structural properties of dense simple liquids are determined predominantly by the repulsive cores;[13,48–51]

b) The hard sphere system can be accurately treated by the Percus–Yevick theory,[52] which turns out to be analytically soluble in this case;[53–55]

c) The properties of the system depend only on a single dimensionless variable $\rho^* = \rho\sigma^3$, where ρ is the number density and σ is the hard sphere diameter.

In addition, there are accurate and extensive computer-simulation results,[56,57] which can be used to refine those of Percus–Yevick theory in the high-density region, where the latter becomes somewhat unreliable.[51,59,59]

There are two main ways of relating the properties of the reference system to those of the system of interest: the variational method and the perturbation method. The variational method is based on the Gibbs–Bogoliubov inequality,[60–62] which may be expressed as follows. If the interparticle potential for the system of interest is $\phi(r)$, which differs from the reference system potential $\phi_0(r)$ by the term $\phi_1(r)$:

$$\phi(r) = \phi_0(r) + \phi_1(r), \tag{21}$$

then the Helmholtz free energies F and F_0 for the two systems at a given density and temperature obey the inequality

$$F \leq F_0 + \tfrac{1}{2}N\rho \int d\mathbf{r} g_0(r)\phi_1(r), \tag{22}$$

where $g_0(r)$ is the radial distribution function for the reference system, and N is the total number of particles. This implies that the "best fit" of the hard sphere reference system to the system of interest may be obtained by minimizing the right hand side of Eq. (22) with respect to the diameter σ. The resulting estimate for the free energy may then be used to calculate all the other thermodynamic properties. This procedure has been applied by Mansoori and Canfield[63,64] and by Rasaiah and Stell[65] to the rare gas liquids and more recently by several workers[66–69] to liquid metals.

The perturbation theory is somewhat more complicated, but has the advantage that it may be systematically improved. There are several variants of the theory,[13] but the most successful appears to be that due to Weeks, Chandler and Andersen.[14,48,49,51,70–73] In this method, one divides the potential $\phi(r)$ into the steep repulsive part $\phi_{\text{rep}}(r)$ and a weak attractive part $\phi_{\text{attr}}(r)$. The difference between $\phi_{\text{rep}}(r)$ and the hard sphere reference potential $\phi_0(r)$ is accounted for by expanding the free energy in the function $\psi(r) = \exp(-\beta\phi_{\text{rep}}) - \exp(-\beta\phi_0)$ and adjusting σ so that the lowest correction to F_0 vanishes. An associated procedure leads to a formula for $g_{\text{rep}}(r)$, the radial distribution function for the repulsive system. The correction to the free energy due to the attractive tail ϕ_{attr} is calculated by the so-called High Temperature Approximation, which amounts to the assumption that $g(r)$ is unaffected by ϕ_{attr}; in this approximation

$$F \simeq F_{\text{rep}} + \tfrac{1}{2}N\rho \int d\mathbf{r}\,\phi_{\text{attr}}(r)g_{\text{rep}}(r).$$

Less simply, but more accurately, ϕ_{attr} can be accounted for by the Optimized Random Phase Approximation.[72,73] This theory has been applied to rare-gas-like systems by Verlet and Weis[51] and shown to be accurate, especially at high densities.

6 THE EXTENSION TO MOLTEN SALTS: CONSTRUCTION OF A REFERENCE SYSTEM

It is clear that in order to extend these theories to molten salts, one needs to define a reasonable reference system and discover its thermodynamic and structural properties. For a reference system to be reasonable, it must satisfy at least three requirements:

a) It must be structurally similar to the real molten salts of interest;

b) Its properties must depend on the smallest possible number of parameters;

c) Its properties must be calculable, or at least representable, analytically.

Requirement a) immediately rules out the use of a neutral hard sphere system as reference. It has long been known from x-ray diffraction studies,[74] and has been confirmed recently by neutron scattering[75–77] and computer simulation,[10,11,15] that a dominant feature of molten salt structure is that of charge ordering: as in the solid, every ion tends to be surrounded by a shell of oppositely charged ions. This important feature will be absent in systems of neutral hard spheres, which therefore form an unsuitable starting point for variational or perturbation procedures.

Bearing in mind requirement b), one is naturally led to consider the system of charged hard spheres, characterized by the charges z_1 and z_2 and the sphere diameters σ_1 and σ_2 of the two components. The properties of this system will depend on four dimensionless parameters: a reduced density, a reduced temperature and the ratios z_1/z_2 and σ_1/σ_2. Obviously, a comprehensive study of this system covering the interesting ranges of all parameters would be a formidable undertaking. However, a good start can be made by considering only the charge-symmetric case, $z_1 = z_2$. In addition, the arguments advanced in the discussion of Corresponding States methods suggest that the influence of the ratio σ_1/σ_2 will be small, unless it deviates greatly from unity. This being so, it will at first be sufficient to confine oneself to the case $\sigma_1 = \sigma_2$, i.e. to the so-called Restricted Primitive Model (RPM).[78-81] Its properties depend on the reduced density $\rho^* = \rho\sigma^3$ and the reduced inverse temperature $\Gamma = \beta z^2/\sigma$, where ρ is the total ionic number density.

From these considerations, it is clear that a knowledge of the properties of the RPM as function of ρ^* and Γ will play a central role in the fundamental theory of molten salts. For orientation purposes, we note that if σ is taken equal to the sum of the ionic radii for K^+ and Cl^-, then at the melting point of KCl we have $\rho^* \simeq 0.69$ and $\Gamma \simeq 52$.

It is now apparent why the theory of molten salts is much more difficult than that of simple liquids:

a) The underlying reference system is characterized by at least two parameters, rather than one;

b) The interaction strength, which may be identified with Γ, is very large (for the simple liquids the corresponding parameter is the ratio of the potential well depth to kT, which is of order unity).

All the recent progress towards a theory of pure molten salts has been progress in understanding the RPM and related models. Since the use of the RPM as reference system requires a knowledge of both its thermodynamic and structural properties, we now review these in turn.

6.1 Thermodynamics of the RPM

At present, the only reliable method of determining both the thermodynamic and structural properties is by computer simulation. The thermodynamic properties are now firmly established over a wide range of ρ^* and Γ, including the molten salt regime, thanks to the Monte Carlo studies of Larsen.[78,79] As we have indicated above, the application of variational and perturbation methods requires not merely numerical values for the properties of the reference system, but a convenient analytic representation of them. This problem has been studied by Larsen,[79] who has derived such a representation for the free energy. This already takes one a long way towards a qualitative theory for real molten salts. Representing the molten alkali halides by the RPM with a hard sphere diameter equal to the sum of the Pauling ionic radii, Larsen[79] has calculated estimates of the internal energies, densities, thermal expansion coefficients and isothermal compressibilities at atmospheric pressure as a function of temperature and made a comparison with experimental results. This comparison is shown in Figures 1 and 2. The agreement obtained, although only semi-quantitative, is extremely encouraging, particularly bearing in mind that the correspondence between the RPM and the real systems has been only roughly made. It leads one to believe that a

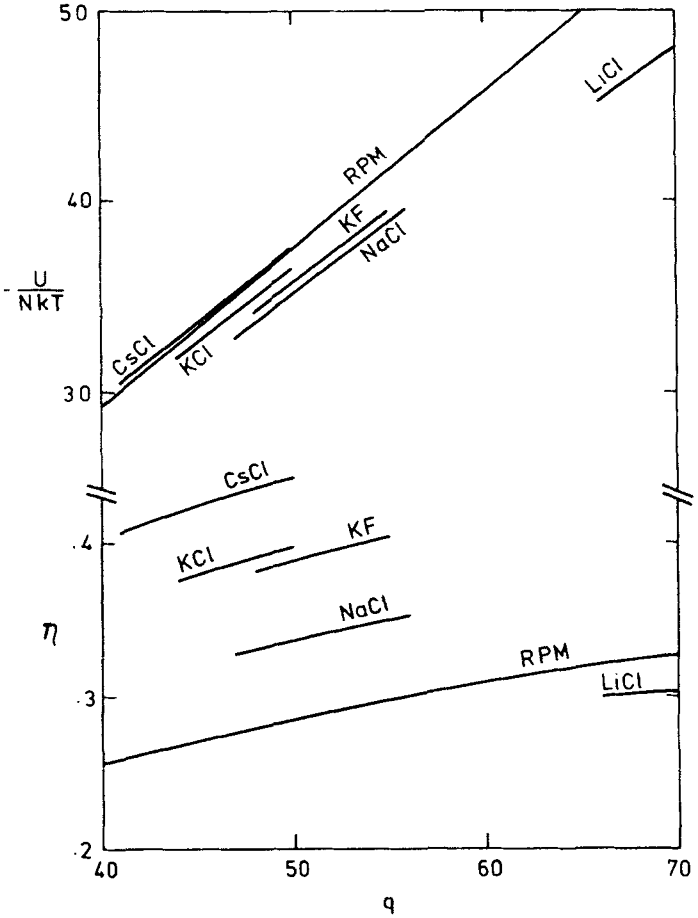

FIGURE 1 Comparison between the Restricted Primitive Model and experiment for molten alkali halides at atmospheric pressure. U is the internal energy for a system containing a total of N ions in volume V. The reduced density η and inverse temperature q are defined by $\eta = \pi N d^3/6V$ and $q = z^2/dkT$, where d, the hard sphere diameter, is identified with the sum of the Pauling anion-cation radii.[101] Reproduced from Ref. 79, with permission.

systematic correspondence based on the use of variational and perturbation methods will indeed be capable of giving a correct description of real molten salts.

In addition to the computer-simulation work, there has also been a sustained attack on the RPM from the purely analytic side. Perhaps the most important single advance here has been the development of the Mean Spherical Approximation (MSA) for systems of charged hard spheres.[80–85]

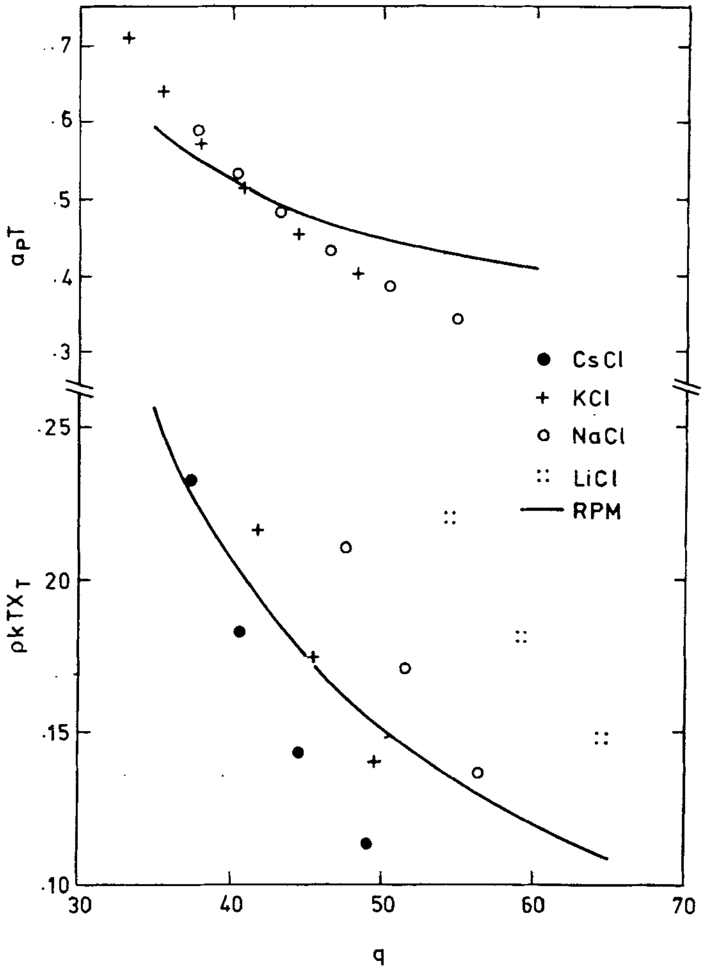

FIGURE 2 Comparison between the RPM and experiment for molten alkali halides at atmospheric pressure. α_p is the expansion coefficient and χ_T the isothermal compressibility; q is the reduced inverse temperature as in Figure 1. Reproduced from Ref. 79, with permission.

This approximation is based on a consideration of the properties of the direct correlation function. If $h_{ij}(r)$ is the total correlation function between species i and j, defined as usual as $g_{ij}(r) - 1$, then the direct correlation function $c_{ij}(r)$ is defined by the Ornstein–Zernike equation

$$h_{ij}(r) = c_{ij}(r) + \sum_l \rho_l \int d\mathbf{r} c_{il}(|\mathbf{r} - \mathbf{r}'|) h_l(r'), \tag{23}$$

where ρ_l is the number density of the lth species. For ionic systems it can be shown[80,86] that the large r form of $c_{ij}(r)$ is

$$c_{ij}(r) \to -\frac{\beta z_i z_j}{r}. \tag{24}$$

The MSA consists in assuming that Eq. (24) is valid as an equality for all r greater than the hard sphere diameter. For the RPM we therefore have

$$c_{ij}(r) = -\frac{\beta z_i z_j}{r} \qquad r > \sigma \tag{25}$$

$$g_{ij}(r) = 0 \qquad r < \sigma \tag{26}$$

the second condition being required by the impenetrability of the cores.

It has been shown by Waisman and Lebowitz[80,81] that the set of Eqs. (23), (25), (26) can be solved analytically to give $c_{ij}(r)$ and the thermodynamic functions. It is found[87] that the internal energy so calculated agrees with the computer-simulation results to about 5 % in the molten salt regime, which is surprisingly good, considering the simplicity of the approximation. Perhaps the most significant feature of the approximation is that it lends itself to systematic improvement. Very recently[88] it has been shown that the first correction to the MSA in a systematic treatment of the RPM already leads to substantially improved agreement with the computer simulation results: in the molten salt regime the internal energy is now in error by less than a percent, which may be considered almost perfect agreement. It remains to be seen whether the theory also gives accurate results for other thermodynamic functions.

An alternative approach to the analytic calculation of thermodynamics of the RPM is through the use of Padé approximants. It has been known for several years[89] that the free energy of ionic systems may be developed as a power series in $\kappa\sigma$, where κ is the Debye–Hückel screening wavevector (in terms of the parameters we have introduced $\kappa\sigma = (4\pi\Gamma\rho^*)^{1/2}$), the zero-order term corresponding to the uncharged system. In view of the very large value of Γ for molten salts, such a development would at first sight appear to be of little use. In particular, the free energy for large Γ is known to be linear in Γ,[87] and such behaviour can never follow from the expansion truncated at any finite order. The solution which has been proposed[87] is to replace the ordinary expansion by the quotient of two polynomials in $\kappa\sigma$ (a Padé approximant), the coefficients being determined by the condition that when the quotient is expanded in powers of $\kappa\sigma$, the appropriate number of terms of the ordinary power series should be reproduced. If the degree of the numerator polynomial is chosen to be greater by two than that of the denominator, the correct behaviour at large Γ will be obtained. Perhaps surprisingly, it turns out that even the simplest Padé approximant gives passable results for the internal energy in the molten salt regime, while the results from the next approximant are accurate to about 2%.

6.2 Structure of the RPM

Although the MSA provides reasonable results for thermodynamic quantities, its prediction of the radial distribution functions for the RPM is rather unsatisfactory: it accounts for the main features of $g_{ij}(r)$,[88,89] but lacks numerical accuracy; in some regions it even fails to satisfy the physical requirement that g_{ij} should be positive. Here again, though, it can be used as the basis for improvements. Since its defects are presumably due to an incorrect modelling of $c_{ij}(r)$ for r just greater than the core diameter, it is natural to attempt a correction in this region. Recently it has been shown[91–93] that if Eq. (25) is replaced by

$$c_{ij}(r) = \frac{K_{ij}e^{-\mu_{ij}r}}{r} - \frac{\beta z_i z_j}{r}, \qquad r > \sigma$$

the approximation remains analytically soluble, at least for the RPM. The parameters K_{ij} and μ_{ij}, of which there are four for the RPM, may be determined by fitting to selected thermodynamic or structural properties; these can be obtained either from Larsen's empirical fit to the simulation results or by the analytic methods described in the previous section. This procedure has been examined recently by Mou and Mazo[93] using the empirical fit and by Larsen *et al.*[88] using the analytic method. In both cases a very substantial improvement in $g_{ij}(r)$ is obtained.

7 FUNDAMENTAL THEORIES: SUMMARY AND FUTURE PROSPECTS

There is at present no complete fundamental theory of molten salts. The approach to such a theory which we have reviewed consists of two stages:

a) The construction of a reference system.
b) The development of a relation between this and real systems.

The first stage is now well under way and, in particular, our knowledge of the RPM in the molten salt regime is becoming fairly complete. However, the second stage has not yet been begun. The most important problem here will probably be the inclusion of a realistic repulsive interaction between ions, since this will have important effects on both the structure and the thermodynamics (it is known, for example, that the repulsive interaction contributes typically 10% to the internal energy in the molten alkali halides).[15,94] The formal generalization of the variational and perturbation methods to two-component ionic systems is straightforward. It does not necessarily follow that the practical application of these methods will be free of problems, or even that the methods will work satisfactorily at all. A study of this question seems one of the most important tasks in the theory of pure molten salts.

We conclude this section by listing some other problems which remain to be investigated.

a) The radius-ratio effect. In some of the alkali halides, e.g. the halides of Li, the ionic radii are so different that short-range repulsion between like ions will play an important role. In such cases it seems unlikely that the RPM will form a suitable reference system; it will be desirable instead to use as reference a system of charged hard spheres in which the two components have different diameters (the Generalized Primitive Model). Here too the MSA is relatively easily solved[83] and it has recently been shown to give a useful description of radius-ratio effects.[82,84,85] However, a computer-simulation study of the Generalized Primitive Model would clearly be very useful, as would further analytic work on its thermodynamic properties.

b) Critical region and vapour phase. Almost everything we have said in this review has referred to the dense molten salt regime. However, there is considerable interest in the properties of molten salts in the critical region and in the vapour phase. The semi-empirical theories have been applied to the study of these states,[20,26,27,43] but there has so far been no proper comparison with (the very limited) experimental information. The fundamental theories seem at present incapable of treating correctly the low density region. For example, the position of the presumed critical point of the RPM is extremely uncertain.[95,96] One of the main reasons for this is that the fundamental theories have not successfully tackled the problem of the low-density clustering of ion.[29]

c) Covalency effects. The fundamental theories will undoubtedly prove themselves first for the alkali halides. But these constitute only a small subclass of molten salts. The extension of these theories to partially covalent salts will certainly be very difficult. (As an illustration of the difficulties, one may cite recent attempts to understand the structure of molten CuCl).[97,100] Here the development of adequate potentials will be a prerequisite.

8 CONCLUSIONS

The theory of molten salts is clearly in a fairly early stage at present. On the one hand we have the semi-empirical theories, which are not properly founded on fundamental principles, but which do have some predictive power. On the other, we have the beginnings of a fundamental theory, which is properly founded, but is not yet practically useful. If one requires to make calculations of thermodynamic properties, the only reliable method is computer simulation[10,11,15,94] and this can only be used if one has a reasonable interionic potential function. If none is available, one is bound to fall back on the semi-empirical methods or corresponding states.

In spite of the present limitations in the theory, there are grounds for optimism. Barring unforeseen difficulties, the variational and perturbation methods based on the Primitive Model of charged hard spheres should soon be in a position to deliver a coherent and accurate theory at least of the alkali halides in the dense liquid region.

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