Molecular dynamics calculations on molten salts

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Since molecular dynamics calculations on liquid systems may be viewed as explorations of the role played by various terms in the intermolecular potential energy, it is particularly suitable for the study of the basic question in fused salt chemistry, namely, what is the role of the coulomb potential? Examples of applications of molecular dynamics studies to equation of state, diffusion, structure and conductivity of fused salt systems are given.

Molecular dynamics, in the context of this discussion, means the detailed calculation of the trajectories of the particles in a liquid. For given potential energies of interaction, high-speed digital computers are used to integrate the equations of motion and to calculate averages of dynamical quantities of interest. Molecular dynamics, therefore, is a systematic exploration of models. In the present case, fused salts, the models consist of the assumptions that the potential energies are those assumed in each case, that classical mechanics is an adequate approximation and that results on short time and short distance scales can be extrapolated to macroscopic behavior. The associated apparatus of computation and of statistical mechanics is firmly based so that it is generally the potential energy functions that are under test.

The special interest of the fused salt chemist is the analysis of the role of the coulomb charges on the static and dynamic properties of the liquid. That is, his questions basically are differential in nature. For example, "How is liquid KCl different from liquid argon?" rather than "Why is KCl a liquid at 1000° and one atmosphere?" "How shall we understand the difference in temperature coefficient of conductivity of KCl and BiCl₃?" or "Why does BeF₂ tend to glass whereas KCl does not?" This differential nature of his questions together with the fact that he is particularly concerned with the effect of one contribution to the potential energy makes molecular dynamics calculations of special interest to the fused salt chemist.

Physical analysis begins with the corpus of data dealing with melting points, boiling points and densities. In addition, heat capacity data lead to the determination of energies and entropies. One enquires as to the role of the charge type, the radius ratio, whether the cation-electron shell is open or closed, the degree of polarizability of the anion, etc.
The molecular dynamics equivalent of this sort of work is equation of state data. Here there are two kinds of calculations. One is concerned with the representation of the properties of a given salt by use of the best available potentials. The second kind of calculation is not meant to be realistic but rather to provide insight by turning on simplified potentials. The prototype of this kind of study is that on a liquid of hard spheres by B. Alder and coworkers. Here one may ask the question "Are attractive forces required for there to be a liquid/solid transition?" Contrary to the intuition of many people, the answer is "No, a fluid of hard spheres has a melting point." It is possible to imagine turning on parts of the potential energy one at a time and enquiring as to the effect of each. Thus, one begins with the hard core, turns on the soft, attractive parts, e.g., in the Lennard-Jones formulation, then the coulombic terms and finally dipolar interactions. At each stage one may compute the equation of state and other properties so as to get some feeling for their relative importance.

A significant by-product of equation of state calculations is the ease with which they may be extended into experimentally inaccessible regions. The computer is indifferent to the actual choice of temperature or pressure so that plausible extrapolations are readily made. Equation of state calculations are best viewed as explorations of the relevant portions of the potential energy diagrams. Comparison with experiment (which often includes data from the solid or gaseous regimes) is really a sophisticated way of studying the potential energy. If this may be taken as known, then extension into regions where experimental data are unavailable may be made with confidence.

Two important points about the potential energy functions which are of current interest are the role of dipole interactions and the extent of deviation from pairwise additivity.

There is reason to believe that ion-induced dipole moments make a small but distinct contribution to the interaction between the ions. Several ways of introducing these forces have been studied. For example, a polarizability term may be added into the potential energy function. The value of the polarizability may be estimated from crystal data, from dispersion measurements, etc. Another method that has been studied recently is the so-called shell model in which polarization is simulated by an artificial construct.4

The nonadditivity is more difficult to deal with. The computational problems, although annoying, are not intractable. The difficulty here is that there is no agreement as to the form to be expected. It has been estimated that nonadditivity may ultimately account for 10-15% of the net potential energy. However, its contribution is concealed in other terms. It is implicit in all data obtained from condensed phases and is not peculiar to fused salt systems.

A particular feature of molecular dynamics calculations is the detailed description they produce of local structure. One convenient
representation of structure is afforded by the pair distribution functions. In their most common form these are graphs of the radial probability density, i.e., the relative likelihood of finding a particle at a given distance from a central particle. There are, of course, four such functions in even the simplest fused salt, namely the ++, --, +- and -- ones, of which three are independent. X-ray scattering data may be used to calculate pair distribution data, but in general the experimental results are a weighted superposition of all of the distribution functions - only the molecular dynamics calculations lead to unequivocal values of the separate distribution functions. With their aid, the average distribution about a given particle can be visualized. Peaks and valleys indicate favored and unlikely positions, respectively. The sequence of peaks reveals a layer structure of alternating charge, rather like the layers of an onion. Fluctuations about the average values are also readily obtained and give information about the stability in time and space of local structures.6

The role of the local structure, as organized by the electrostatic field, can be seen clearly in an investigation of a model of K2MgCl4 where only central (i.e., nonchemical) forces are utilized. In an earlier report7 we noted that a highly structured system was found based on a coordination of three Cl- around the central Mg++. More recently, we have observed that this coordination number is very sensitive to the size of the Mg++. An increase in the effective repulsive radius from 0.85 A to 1.0 A causes a decisive shift in the coordination from three to four - the fluctuation around the value in each case is remarkably small. The coordination number arises entirely out of packing problems associated with the centro-symmetric potentials and has nothing to do with the "chemical character" of Mg++ or Cl- since none is employed in the model. The structures thrown up by this sort of calculation may be capable of producing Raman lines. The autocorrelation function of the polarizability of a volume of the fluid is involved and interesting questions as to the way in which the symmetry properties of the fluctuating force should be dealt with. It is a truism that diffusion coefficients tend to be of the order of 10^-5 with apparent activation energies of 3-5 kcal. Fused salts are no exception in this regard. That is, the coulomb potential plays a negligible role in ordinary diffusion. Nevertheless, there is an important way in which diffusion in fused salts differs from that in uncharged systems. The pair distribution functions reflect the fact that the coulomb forces heighten the probability of oppositely charged ions to be near neighbors and depress the probability of like charged ions to be adjacent to each other. This means that the probability of a diffusive encounter between two cations is considerably reduced below that of such an encounter between an anion and a cation. The diffusion process over long distances is unaffected by these considerations - it is only when the distances become very short that these considerations appear.

A schematic representation of the situation is given in Fig. 1. It emphasizes that the probability of an encounter of a given sort

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depends not only on the bulk diffusion coefficient but also on the values of pair distribution functions at the chosen collision radius.

Two experimental situations in which this effect is important have been studied in our laboratories. One is the spin-spin interactions between paramagnetic ions in tetrabutylammonium tetrachloromanganate/tetrachlorocadmate melts. Here the dipole-dipole coupling between the anions can be measured directly and compared with the measured tracer diffusion coefficients.

In the other experiment, photo-excited anions are stimulated to radiationless deactivation (quenched) by encounters with various other ionic species, the rates of deactivation deduced on the basis of diffusive encounters being compared with the experimental ones. Both cases give clear-cut indications that local diffusion is significantly different from bulk diffusion.

A way of dealing with this problem is to consider that the pair distribution gives rise to a so-called potential of average force which may be utilized in the diffusion equation in the same way that, e.g., gravity might be introduced. One form of this modified diffusion equation is the Smoluchowski equation:

\[
\frac{\partial c_i}{\partial t} = \nabla \cdot D_i (\nabla c_i + \frac{c_i}{kT} \nabla \phi_i) = \nabla \cdot D_i (\nabla c_i - c_i \nabla \ln g_{11}(r))
\]

In order to examine this situation more closely we have carried out a molecular dynamics simulation of a quenching experiment. Each ion is considered to be photoactivated (i.e., labelled) initially. The rates of first encounter of a representative central ion with other ions of the same or opposite charge, respectively, are accumulated. In this way either the diffusive fluxes or the instantaneous concentration profiles can be computed and compared with various analytic expressions. These results are preliminary in that longer runs (which are now in progress) are required in order to improve the statistics. Nevertheless, it is easy to see from Fig. 2 that the coulombic attractions and repulsions produce substantial differences in the (++) and (+-) encounter rates.

The physical property most characteristic of a fused salt is its high electrical conductivity. The equivalent conductivity commonly is distinctly larger than that in the corresponding aqueous solution - allowance must be made for the fact that the ions are not hydrated, that the temperature is higher and that the frictional resistance arises from other ions entirely rather than mainly from a dipolar solvent. Phenomenological discussions of transport properties frequently cast the problem in terms of the balance between applied forces, e.g., electrostatic and frictional resistance. If the forces are taken as known, there remains the determination of the effective frictional force. If the frictional force in electrical conductivity is taken to be the same
as that in diffusion, the Nernst-Einstein relation results. If the frictional forces in diffusion and viscous flow are taken to be the same, the Stokes-Einstein relation results. It is not always sufficiently recognized that the equating of the forces is not all that is involved since the local forces must also be known. That is, in electrical conductivity the local force is less than the applied electrical field because of the polarization of the medium and, consequently, deviations from the Nernst-Einstein relation may, in part, be attributed to the effect of the medium on the electrical field. Nevertheless, a molecular explanation of deviations from these relations in fused salt systems has long been a central problem in fused salt chemistry.

Some of the questions which arise naturally are: How does the internal resistance depend on the size, charge type, polarizability, temperature, etc. of the melt? To some extent, conventional experimentation provides answers to questions of this sort. More difficult are the questions which are concerned with the mechanism: Why and how are the resistances to viscous flow and diffusion related to those in conduction? How do the positive and negative ions move with respect to each other, i.e., are there relative rotations, paired jumps, or a biased "rattling" motion? What determines the relative transference numbers and are they reliable indicators of complexation? Why does isotope separation occur? What happens at high fields? Problems of this sort fall naturally into the purview of molecular dynamics calculations and valuable beginnings have been made in answering some of them. Hansen and McDonald have reported as separation of the velocity correlation functions, isolating the cross-correlation terms which are responsible for the deviations from the Nernst-Einstein relation. We have examined the K₂MgCl₄ system, obtaining values for the relative transference numbers of the ionic species by the applied field method (see below). At 1100°K, the transference numbers of the cations with respect to the anion were found to be 0.2 for Mg⁺² and 0.8 for K⁺. These are in reasonable agreement with experiment and reflect the fact that the Mg⁺² is much more highly coordinated by Cl⁻ than is the K⁺.

The calculation of electrical conductivity has been approached thus far in three different ways. The autocorrelation function for the electrical current (which may be decomposed into velocity correlation functions) can be related to the conductivity by Kubo-type relations. A second, quite novel method is to treat the electrical field as a perturbation on the trajectories of the particles, comparing their motion with and without the field (which may be either a step function or an impulse). Comparison of the two sets of data leads to estimates of the electrical conductance. Finally, there is the "brute force" method. Remembering that the motion produced by the field is a small perturbation on the Brownian motion, it can be seen that very high external fields can be applied without substantially modifying the gross behavior. In a computer experiment, millions of volts per centimeter can be applied without concern about electrode problems and thermostating can be supplied to deal with heating. Consequently, one can explore the very high
field region and determine the range of validity of the linear current/voltage relations. In experiments of this sort in our laboratories, we have observed the high field conductance of a model of KCl in the vicinity of $10^6$ volts/cm.

It is to be expected that calculations of this sort will be widely extended.

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Fig. 1. The probability of an encounter between two ions depends not only on the long range diffusion process (upper figure) but also on the pair distribution function at the chosen collision radius (lower figures).

Fig. 2. The rate of quenching of positive and negative ions, respectively, by a central positive ion. Model is KCl at 1098°, utilizing Tošić/Fumi potentials and an assumed collision radius of 2.0 Å.