

Theoretical studies of aqueous solution structure

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Abstract - Computer simulation and, more analytical, integral equation methods can be applied to the problem of elucidating the detailed structural properties of strongly interacting molecular solutions of genuine chemical significance. The more analytical, extended RISM, approach can provide such results in a computationally convenient way not yet available via simulation. The success of such current statistical mechanical approaches in describing aqueous solutions is considered through three examples: the structure of liquid water as a function of hydrogen bond strength, the potential of mean force between atomic ions in an aqueous medium, and the aqueous solvent effect on the reaction free energy surface for the S_N2 reaction of chloride with methylchloride.

INTRODUCTION

The description of solutions of chemical interest at a molecular level is of wide interest for the interpretation, and prediction, of experimentally observed phenomena. Examples of such phenomena include the structural interpretation of scattering results for molecularly complex neat liquids, the relative spatial distribution of solutes in dilute solution, and solvent effects on chemical reaction rates and pathways.

Rapid advances continue to be made in the theoretical area which now permits the study of such phenomena in increasingly more complex systems. Hence, many systems of genuine chemical relevance are within reach of present capabilities. The development of model interaction potentials for molecular solution components, which are at the same time relatively simple in form and reasonably faithful in reproducing such interactions, has played a major role in this progress. In parallel, new techniques for computer simulation of large liquid systems have emerged, and the accessibility to researchers of appropriate computational resources has been rapidly enhanced. Such simulation studies can now provide enormous detail on molecular structure and dynamics in liquids. For pure liquids, such calculations can be reasonably described as routine.

For solutions, substantial progress is being made using computer simulation, but such calculations are far from routine. They have enormous computational requirements, frequently in the hundreds of hours of conventional main-frame time. Therefore, there is substantial motivation to develop more analytical methods which can be used to obtain useful structural information in a relatively straightforward and inexpensive way. The demands on such a theory are severe, due to the delicate balance, in strongly interacting systems, between repulsive molecular packing forces and strong attractive polar forces. Nevertheless, reasonable techniques have emerged for tackling such systems. It is the primary emphasis of this contribution to discuss recent structural results for chemical systems of current interest, and the role which more analytical theories can play in exploring the behavior of such systems.

The technique of primary interest here is the so-called RISM integral equation method (1-4) which we have shown to be a valuable tool for the study of strongly interacting molecular liquids. For the cases to be considered here, computer simulation results are also available providing a test of the accuracy of the approach.

In the next section we outline the methods used in such calculations. We then consider three examples of interest. These are the structure of pure liquid water, the interaction of atomic ions in aqueous media, and solvent effects on the free energy surface for a chemical reaction in water.

METHODS

I comment on models first and then on how these models are treated theoretically.

To realistically model complex molecular liquids, the form known as an interaction site model (ISM) has been almost exclusively adopted (5-8). Such an intermolecular potential between two molecules is expressed as a sum of spherically symmetric potential functions, each dependent only on the distance between a distinct pair of sites, one in each molecule. Such sites are frequently specified by the nuclear positions of the component atoms, but this is not necessary. For a pair of molecules, labelled by M and M', the ISM potential has the form

$$U_{MM'}(\{r\}) = \sum_{\alpha_M, \gamma_{M'}} u_{\alpha_M, \gamma_{M'}}(r_{\alpha\gamma}) \quad (1)$$

Here, r denotes the full translational and orientational set of intermolecular coordinates, α_M labels an interaction site (e.g. atom) in molecule M and $r_{\alpha\gamma}$ is the distance between site α_M and site $\gamma_{M'}$.

The individual terms in the intermolecular potential are typically composed of a short-ranged, primarily repulsive, "core" potential (exponential or Lennard-Jones 6-12 form) and a Coulombic term. Hence, the total intermolecular potential incorporates realistic molecular shape through the superposition of the atomic cores, as well as an electrostatic potential; the latter can successfully mimic both long-range low-order multipolar interactions and the detailed dependence required at short intermolecular separations.

The advantages of the ISM form of the potential are several. First, it is empirically clear that such a form can provide a good description of a wide variety of real molecular liquids (5-8). Second, there is substantial evidence that potential parameters developed in this format are largely transferable from one molecule to another if the sites are identified with chemically distinct atomic types, which are familiar chemical entities (5-7).

From a theoretical viewpoint, this form also has advantages. In computer simulation studies (9,10), such a potential can be evaluated rapidly, which is a major consideration in such numerically intensive work. In more analytical approaches, the ISM format allows the implementation of the RISM-type integral equation methods (1-4,11) discussed below.

Simulation of liquid structure, in principle, provides the exact result for a given model. Hence, it can provide, first, results essential for the testing of more analytical approaches or, second, an unequivocal test of the validity of a model when comparison is to be made to experiment. The two major approaches to simulation are the Monte Carlo (9) and molecular dynamics (10) methods, and both have been used in calculations discussed below. In all cases, one explicitly produces a large set of molecular configurations, which are representative of the system of interest, by explicitly sampling molecular coordinates for a group of molecules interacting via the specified model potential function.

In contrast to simulation methods, the techniques classified as integral equation methods are analytically-based. The results derivable are characteristic molecular spatial distribution functions for component-relative coordinates, and thermodynamic properties derivable from them. The solutions to these equations are typically obtained numerically; I will not discuss these solution techniques here.

The class of equations designed for implementation with interaction site models yields the relative intermolecular distribution of pairs of sites, which is an isotropic function dependent only on the site-site separation. This type of equation is usually referred to as a RISM (reference interaction site method or model) equation (12), for historical reasons, and is not restricted to rigid molecules or to those of relatively high symmetry. The solution of the equations provides a description of liquid structure through the pair correlation functions. For a pair of molecules, labelled by M and M', and assuming an isotropic fluid, the molecular pair site-site correlation function, $g_{\alpha_M \gamma_{M'}}(r)$ is simply the relative probability of finding the intermolecular site pair with the distance specified by r , compared to that in a corresponding fluid having no intermolecular spatial correlations. The quantity $h_{\alpha_M \gamma_{M'}}(r) = g_{\alpha_M \gamma_{M'}}(r) - 1$ is simply the excess (or deficit) with respect to unity in this relative probability.

The intermolecular site-site correlation function is composed of an infinite sum of terms, each of which is representative of a particular path connecting the site pair of interest through the fluid. These paths are prescribed by connections through intramolecular correlations between sites in the same molecule and intermolecular site-site interaction potentials. A particular example of such a term is shown schematically in Fig. 1 for a set of diatomic molecules. Here the dashed lines represent interaction potentials and the wavy lines represent intramolecular correlations. The sum of all such terms results in the total intermolecular correlation between the sites marked by the stars.

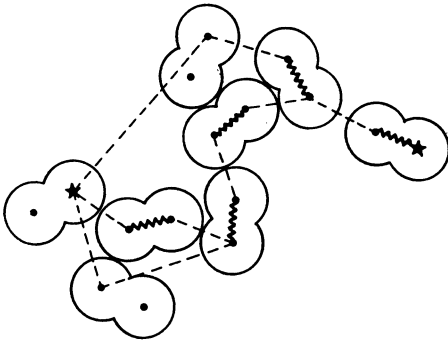


Fig. 1. Schematic representation of a term in the intermolecular site-site correlation function for an ISM liquid.

An integral equation which provides an approximation to the sum of these terms and which is of central interest here is the so-called RISM equation

$$h_{\alpha_M \gamma_{M'}} = \sum_{\delta, \lambda} \omega_{\alpha_M \delta_M} * c_{\delta_M \lambda_{M'}} * \omega_{\lambda_{M'} \gamma_{M'}} + \sum_{M''} \sum_{\delta, \gamma} \omega_{\alpha_M \delta_M} * c_{\delta_M \lambda_{M''}} * \rho_{M''} h_{\lambda_{M''} \gamma_{M'}} \quad (2)$$

where '*' denotes the spatial convolution integral over intermediate coordinates and c is the so-called site-site direct correlation function. Here ω denotes the total intramolecular equilibrium site-site pair correlation function,

$$\omega_{\alpha_M \gamma_{M'}}(r) = \delta_{\alpha\gamma} \delta(r) + (1 - \delta_{\alpha\gamma}) s_{\alpha\gamma}(r) \quad (3)$$

where $s_{\alpha\gamma}$ is the equilibrium pair correlation function between distinct sites in the liquid state.

Iteration of Eq. (2) for h in terms of ω and c shows that the site-site intermolecular correlation functions which follow from the RISM equation correspond to "chains" of direct correlation functions of all possible lengths, with intramolecular correlations (ω) inserted between the intermolecular c 's; the factors of ω carry correlation through molecules, and the c 's transmit the information through the fluid, between molecules.

The RISM equation defines c , in terms of h and ω , and a closure relating c to h is required to produce a useful theory. The direct analogues of the so-called hypernetted chain (HNC) and Percus-Yevick (PY) closures have been demonstrated by example to be very productive for the description of structure both in non-polar and in strongly polar dense liquids (1-4,11). In the polar case, an explicit "renormalization", or screening, of the Coulombic interactions can be carried out formally at the outset (1), in analogy to Debye-Hückel theory in electrolytes. Hence, in this so-called "extended RISM" approach, only screened, and therefore short-ranged, interactions must be dealt with in further theoretical study.

It has been found that an HNC analogue is an appropriate closure for the highly polar case. This can be rationalized by noting that in the limit that all intramolecular bonds are removed the system reduces to a dense ionic fluid for which HNC is known to be a productive approach (13). In the absence of Coulombic terms in the ISM, the equations become equivalent to the RISM equation with HNC-like closure, which generally produces good results for completely non-polar systems (14). It is the results from the extended RISM equation that I consider in the next section.

STRUCTURAL RESULTS

Pure Water

I consider the results obtained for pure liquid water (1g/cc, 298K) first. Here, I concentrate on the results obtained via the extended RISM theory, first, to show that it is a viable approach for complex, strongly interacting, liquids and, second, to examine some characteristics of water structure per se as it relates to the strength of the hydrogen bond interaction (2).

Although the molecular shape of a water molecule is basically spherical, the polar forces are strong and directional. It is widely appreciated that the double donor-acceptor hydrogen bonding character produces (under the usual ambient conditions) a liquid structure which retains a resemblance to ice I (15). In particular, the nearest neighbors tend to be tetrahedrally disposed around a water molecule, rather than being nearly close packed as in simple liquids, so that the number of such neighbors is about 5.5, as opposed to about 12 in the latter case. This ice-like bonding pattern extends distinctly beyond nearest neighbors;

in the oxygen-oxygen correlation function a distinct second nearest-neighbor peak is apparent at a distance characteristic of a tetrahedral O-O-O angle. Nevertheless, it is clear that packing and directional hydrogen bonding compete in liquid water structure, and the degree of distortion of hydrogen bonding depends on this competition.

To see this, I consider here results for two very similar models, the so-called TIPS and SPC models (8). Both include a single Lennard-Jones sphere centered on the oxygen atom and three partial electrostatic charges located at the nuclear positions. The charge on oxygen $q_O (= -2q_H)$ is about -0.80 in both models. The results from computer simulation for TIPS (6) and SPC (8) show structural results which are quite similar, although the SPC model reveals the small but distinctive second-neighbor peak in g_{OO} ; for TIPS, the O-O function is essentially flat at this distance. An explanation for the latter fact will be clear from the discussion below.

Figure 2 shows a comparison of the correlation functions from a computer simulation of TIPS water (5) with the extended RISM result for the same model.

As can be seen from these results, the agreement is qualitatively good. Only for the shortest O-H distance is there a major discrepancy; the directly hydrogen-bonded atomic pair give rise to a peak which is too sharp and narrow and occurs at somewhat too small a distance. The number of H atoms involved in this peak is, however, approximately two, as expected (2).

The growth of ice-like correlations with hydrogen-bonding interactions can be seen by carrying out a gradual increase in the electrostatic partial charges in a model which mimics water. This has been carried out using the extended RISM approach (2) and the results are shown in Fig. 3. Here we consider the SPC model, but for scaled site charges ranging from approximately 25% to about 110% of its ideal model value. The arrows indicate the direction of change of the amplitude of the atom-atom correlation function with increasing polarity.

For correlation functions involving H, the distances corresponding to the distinct peak positions inside 5\AA are identifiable in an idealized dimer geometry. These correlations show qualitative change with polarity, but the distinct peaks seen correspond to distances between nearest neighbor molecular pairs; the behavior is indicative of distinct molecular pair orientational preferences.

The O-O function shows the distinctive behavior of water. As polarity increases, the first peak, corresponding to neighboring pairs, shifts to somewhat smaller distance and narrows, the latter effect resulting from a decrease in coordination number as the relatively open bonding structure is formed. Peculiar to water is the gradual growth of the peak at about 4.5\AA , indicative of a significant population of second neighbors at the characteristic distance for a tetrahedral O-O-O angle. Correspondingly, the peak at about 6\AA , which is characteristic of a nearly linear O-O-O arrangement in the non-polar liquid, decreases gradually. The resulting structure appears at any point during the charging process to be a mixture of structures which are increasingly weighted toward tetrahedral coordination and away from the packing-dominated simple liquid structure. Hence, it follows that the lack of a distinct second-neighbor peak for TIPS water is only representative of a slightly under-developed correlation.

Solute-solute interactions

Probably of most interest to chemists in the context of liquids is the interaction of molecular solute components in a solvent medium. The calculations of interest here focus on the so-called potential of mean force, or solvent-averaged, potential. The relative values of the potential of mean force for different fixed solute configurations are simply equal to the relative free energies associated with those configurations in a solvent bath; the solvent is implicitly averaged over all of its configurations.

Of primary interest is the interaction of species at short range, since it is at long range that continuum solvent theories employing empirical macroscopic solvent properties pertain. In contrast, at short range, the details of molecular packing and polar interaction potentials are presumably critical to the forces on solutes. Further, the behavior in dilute solution is of first concern, since only with such information can one disentangle the influence of the solvent alone from modifications of the solvent associated with finite concentration effects.

Using special sampling techniques, the potential of mean force for an isolated solute pair is accessible via computer simulation (16).

Nevertheless, such calculations remain extremely time consuming and it is in such cases that more analytic, integral equation, approaches become most valuable. Computation times for such calculations are presently roughly two to three orders of magnitude less expensive than the corresponding simulation, so that systematic studies become totally accessible.

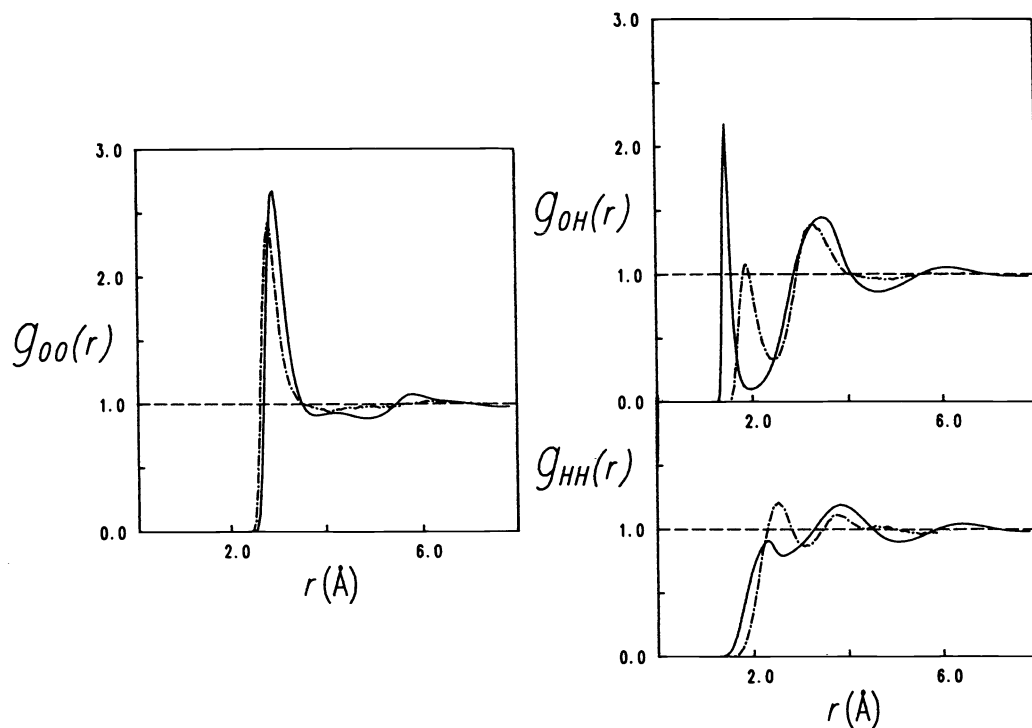


Fig. 2. Site-site correlation functions for TIPS water. Extended RISM (—), simulation from Ref. 6 (---).

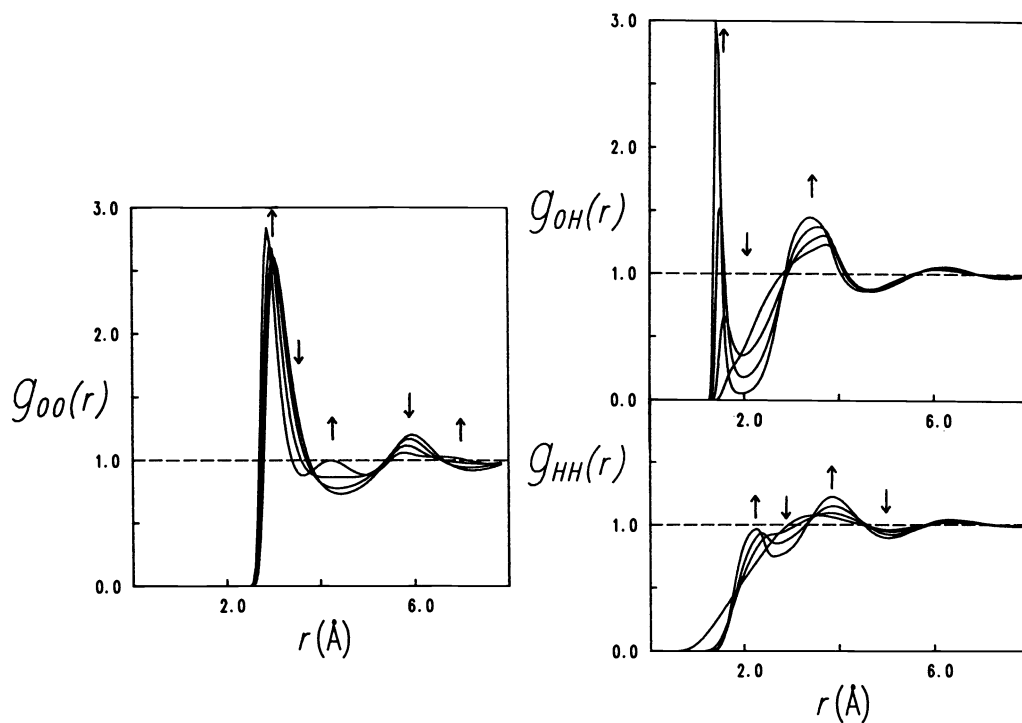


Fig. 3. Site-site correlation functions for SPC-like model of water for scaled site charges. Arrows indicate the direction of change for increasing charge. Values for curves shown (in units of e) are $Z_H = 0.1, 0.25, 0.35, 0.45$.

Results for alkali halide ion pairs in water have now been obtained using computer simulation (16), and both extended RISM (17) and traditional (angular expansion) molecular integral equation (18) methods. The first two, discussed here, have employed effective potentials formulated as an ISM, while the last has been based on a water-like multipolar model. It will be of interest to compare the results of these detailed studies with so-called solvation shell or Gurney models (19). Such models invoke the picture of a perturbed solvent layer surrounding the solute and assign a proportional free energy to the volumetric loss of perturbed solvent to the bulk, which results from overlap of such regions by close approach among solute pairs. The potential of mean force for $\text{Na}^+ - \text{Cl}^-$ which fits the thermodynamic results for relatively dilute solutions is shown in Figure 4 along with the corresponding continuum model. The continuum model assumes that the solvent contribution to the potential of mean force leads only to a reduction in the Coulombic interaction between ions by a factor of the bulk solvent dielectric constant.

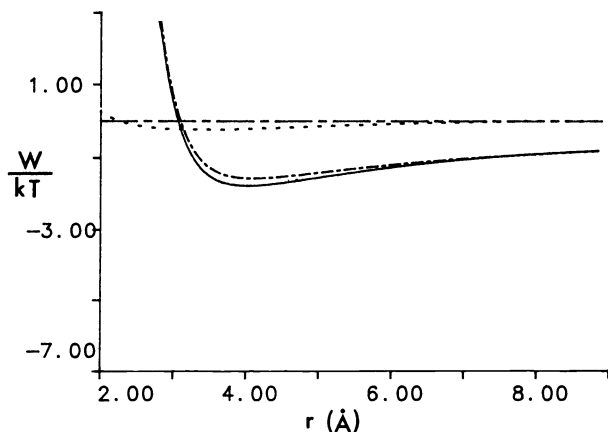


Fig. 4. $\text{Na}^+ - \text{Cl}^-$ potential of mean force. Continuum solvent (---); solvation shell model (—); shell model perturbation term (-.-).

As was pointed out by Friedman some time ago (19), it is somewhat remarkable that such small differences from the continuum model are sufficient to account for the experimental thermodynamics. Correspondingly, it follows that the thermodynamics are necessarily sensitive to rather small inaccuracies in the effective potential, so that success or failure in comparison with experiment for such quantities is clearly a poor test of the veracity of the qualitative features of the potential.

I now consider simulation (16) and extended RISM (17) studies of this same potential of mean force. The simulation studies are carried out with recent ion-water and water-water effective pair potentials from Jorgensen's laboratory (20), and yield the relative probabilities of ion pair separations for interionic center-to-center distances from about 2\AA to 6\AA . Hence the resulting potential of mean force includes an undetermined absolute constant. The values also retain statistical uncertainty of about 0.5 kcal/mole at each distance. The extended RISM calculations are carried out with the three site TIPS model for water (6) and ion-water potentials (17) which are fit (via the ion-water core interaction parameters) to experimental ion-water interaction energies and idealized geometries from ab initio quantum calculations. Of most importance, the continuum solvent contribution is obtained from the phenomenological dielectric constant so that only the corrections to the continuum theory are required from the RISM theory, as described elsewhere (21).

The results of these detailed model studies are in general accord with one another, although the details of the models differ sufficiently that a quantitative comparison among the results cannot yet be made. The most significant qualitative features are apparent by comparing these results and the corresponding continuum solvent model. Such a comparison is shown in Fig. 5 as a function of ion separation for an $\text{Na}^+ - \text{Cl}^-$ ion pair in water at 25°C . The dashed line is the extended RISM result, while the heavy solid line is from the published simulation studies. The narrow solid curve is the continuum solvent model.

As is clear from the figure, there are at least two significant minima in the solvent-averaged potential, one at ion contact and one for a solvent separated ion pair (at $\sim 4.5\text{-}5\text{\AA}$). These are separated by a significant ($\sim 2\text{-}3 k_B T$) free energy barrier. Comparing to the continuum model, there are two points of special interest. First, there is (necessarily) a single minimum for the continuum model, and this occurs in approximately the same location as the barrier in the molecularly detailed treatments. Second, the actual distance of ionic "closest approach" (e.g., the smallest distance where the potential energy is still negative) is substantially smaller than for the continuum case, a fact of significance in such contexts as ion spin relaxation or ionic reaction rates. By further analysis of these results (17), it can be shown that the force producing the additional attraction in the potential of mean force, over the continuum model, at short distance resides primarily in the

molecular solvent entropy gain associated with ion pairing, while the barrier between minima is primarily energetic in nature. We also note that despite the striking difference between the extended RISM and solvation shell model potentials of mean force (Fig. 4) the two sets of potentials are found to be equally compatible with low concentration thermodynamic data for NaCl solutions (17).

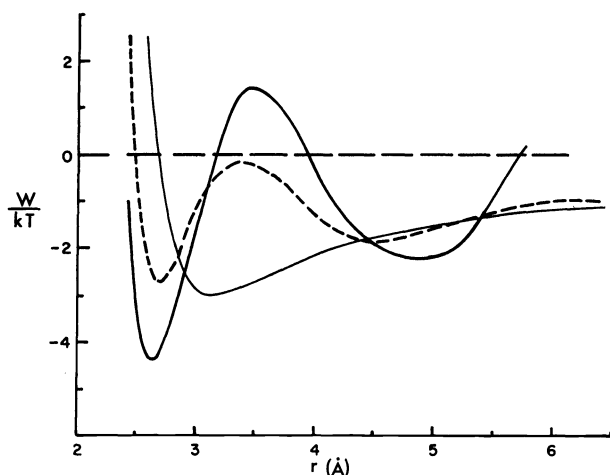


Fig. 5. Potentials of mean force for $\text{Na}^+ - \text{Cl}^-$ ion in water, 25°C.

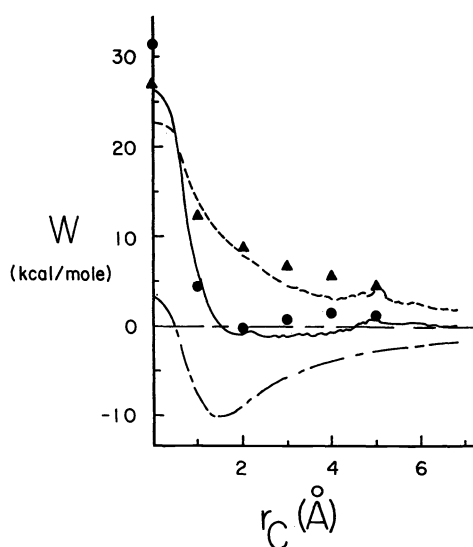


Fig. 6. Comparison of extended RISM and simulation (4) for reaction free energy surface at 25°C. Gas-phase potential (—); solvent contribution, MC (---), RISM (\blacktriangle); total free energy, simulation (\longrightarrow), RISM (\bullet).

A related, but more demanding, calculation is required for treating the free energy associated with chemical reactions in solution. The quantity of interest here is also a potential of mean force, or free energy, associated with the sequence of configurations describing the reactants as a function of reaction coordinate. In addition to the relative structural complexity of such a "solute", the solvent-solute interaction potentials in general depend on the reactant geometry, due, for example, to charge migration within the reactant complex in passing from reactant to product states.

Only recently have calculations of a reaction free energy surface in solution been carried out (4,22); Jorgensen's laboratory has considered symmetrical $\text{S}_{\text{N}}2$ reactions of Cl^- with CH_3Cl in water (22). This work has involved quantum chemical calculation of gas phase potential surfaces, corresponding evaluation of appropriate reactant-solvent ISM potential functions, and a computer simulation evaluation of the solvent induced modifications to the gas phase energy surface.

The solvent contribution to this potential of mean force is accessible to the extended RISM approach and this calculation has been carried out (4). The details are described in the cited reference. The model used in this calculation assumes a somewhat simpler ISM than that employed in simulation, but these simplifications should not change the free energy qualitatively. The reaction is considered only for collinear $\text{Cl}-\text{C}-\text{Cl}$ and has been evaluated as a function of the reaction coordinate r_{C} developed earlier (22) and given in terms of atomic coordinates by

$$r_{\text{C}} = |r_{\text{C}} - r_{\text{Cl}'}| - |r_{\text{C}} - r_{\text{Cl}}| \quad (4)$$

where Cl denotes the attacking ion and Cl' the leaving group. The (symmetric) transition state occurs at $r_{\text{C}} = 0$. The overall symmetry of the collinear case implies that only values ranging from $r_{\text{C}} \rightarrow \infty$, widely separated reactants, to $r_{\text{C}} = 0$ are of interest, with the separating products following the same free energy surface in reverse. The extended RISM results at representative points and the Monte Carlo results are shown in Figure 6, at 25°.

It is clear that the new results follow the Monte Carlo simulation rather well and manifest a dramatic solvent effect on the reaction surface. The RISM theory yields a barrier height of 31 kcal/mol, slightly larger than the Monte Carlo and apparent experimental results of 26.3 and 26.6 kcal/mol, respectively. Also in accord with the Monte Carlo results, the ion-

dipole potential minimum is substantially flattened by the solvent, with the potential becoming slightly repulsive further along the reaction coordinate. These results, obtained with RISM for a small fraction of the computational effort of the simulation work, provide a strong impetus for further application to reacting systems, as well as to conformational equilibria. Such studies are currently underway.

CONCLUSIONS

It is clear that theoretical studies of solutions can now make significant contributions to the description of systems of genuine chemical interest. Reasonable models are available for the description of the interactions among molecular solution components and the statistical mechanical techniques are available to develop the structural implications of these models. In particular, non-simulation methods are a very promising source for semi-quantitative results which can be obtained relatively rapidly and hence routinely. Both simulation and more analytical approaches will certainly play increasing roles in the description of molecular structure in complex chemical solutions in the future.

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