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The quest for the structure of water and aqueous solutions

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Abstract. During the past 25 years neutron diffraction has made a major contribution to understanding the microscopic structure of water and aqueous solutions. By performing isotope substitution on specific atomic sites, it is possible to develop a comprehensive picture of the way water molecules organize themselves around the ions and molecules which dissolve in or mix with water. The resulting data provide a sensitive, sometimes controversial, test of existing theories of the aqueous systems, which due to their complexity at the microscopic level, can normally only be derived using computer simulation techniques. This paper reviews some of the recent achievements in the field of neutron diffraction from aqueous systems and suggests how future experiments might be interpreted with the aid of computer simulation techniques.

1. Introduction

The importance of water in our environment can hardly be over-emphasized: its properties have largely determined the evolution of life on Earth as we now perceive it, and water is ubiquitous in all aspects of human endeavour. The large amount of enthalpy, 41.5 kJ mol^{-1} , which is released when water molecules in the vapour state coalesce to form a droplet is a major driving force behind many of the weather systems that travel through our atmosphere (Gibson 1963), and, as we now know, the state of the climate has had a strong influence on the development and evolution of biological organisms. If that energy of fusion were significantly different it is unlikely the world would be as we now find it. Other unexpected properties, such as the fact that ice is less dense than water and the fact that the temperature of maximum density of water is above its freezing point, are crucial to the evolution and survival of much of the fauna in the world around us. Therefore it is not surprising that the study of water and its solutions has taken on special significance: there is apparently no other medium quite like water.

Historically, water was studied with x-rays by Morgan and Warren (1938), and later by Narten and Levy (1969). The primary conclusion from that work was that water was tetrahedrally bonded in a manner not dissimilar to that occurring in hexagonal ice. Yet this quasi-crystalline view of water was unsatisfactory, for it did not account for the lack of long-range order in the liquid, and it was necessary to contrive ‘interstitial’ molecules in the lattice to account for the experimental data quantitatively.

The early 1970s saw something of a breakthrough in understanding the structure and dynamics of water. Based on earlier ideas for a water potential it became possible to perform a computer simulation of water (Barker and Watts 1969, Rahman and Stillinger 1971) which reproduced qualitatively the structure and dynamics of water as far as they were known at the time: there was no need to make assumptions about local or longer-range quasi-crystalline order.

Almost simultaneously with this development of computer simulation methods, the advent of intense neutron sources, such as that of the Institut Laue Langevin at Grenoble in the early 1970s, meant that experiments to extract specific site–site radial distribution functions in water and aqueous solutions were achievable for the first time, using the newly discovered technique of isotope substitution (Enderby *et al* 1966, Neilson and Enderby 1983). The advent of intense *pulsed* neutron sources, such as ISIS, has meant that the technique of hydrogen–deuterium substitution has become a routine tool for atomic scale structure studies (Soper and Silver 1982). These experiments have provided a crucial test of, and control on, the many interatomic potentials for water and aqueous solutions that have been developed over the years, and this interplay between experiment and computer simulation has continued to the present day.

John Enderby did much of the pioneering work with neutron diffraction and isotope substitution while at Sheffield University. In 1969 he moved to Leicester and expanded the investigations to include molten salts and aqueous solutions, and it was soon after this that he published the little monograph *Delight in Disorder* (Enderby 1970). This was an account of his inaugural lecture at Leicester on 13 November 1969. It is in fact a quite brilliant summary of why it is that we study liquids and the disordered states of matter.

The context of *Delight in Disorder* is of course liquid metals and binary alloys: that was the hot topic of the day and the area where John, as a young researcher at Sheffield, had already made a major contribution, but if I quote a passage from the middle of the lecture, I think you will get some idea of the prophetic nature of John's vision:

...neutron scattering is really a nuclear process so that by intelligent use of isotopes quite different scattering patterns from the same liquid can be obtained. In principle this approach can be applied to a wide variety of liquids—water, CCl₄, aqueous solution, etc. In practice such measurements present quite severe experimental problems and are only in their infancy. What little is known, however, already points to the great usefulness of the concept of 'partial' structure factor. I imagine that these methods will find considerable application in the coming years, particularly from both a chemical and a biological point of view.

In the third (undergraduate) year at Leicester I did a project under John's supervision: *X-ray Diffraction of Water and Aqueous Solutions* (unpublished). Even in 1972 this kind of experimentation was extremely tedious and highly non-automated, requiring the developing of photographic plates and laborious measurements with a densitometer. The results were never published, but were nonetheless quite intriguing: the position of the main diffraction peak from a solution of sodium chloride in water moved to larger Q values as the concentration of the salt increased (table 1). For nickel chloride solutions however the peak started to move back to lower Q values as the concentration increased still further. However because there are so many different contributions to the x-ray diffraction pattern from an aqueous solution it was not possible to assign the movement of this peak to any particular structural feature. The same effect was observed in some of the first neutron diffraction experiments on aqueous solutions (Enderby *et al* 1973), but it was only recently that, using H–D substitution on the water protons, we were able to resolve the issue by demonstrating that this peak shift corresponded to a very real 'electrostriction' of the water structure by the dissolved ions, and that the change in water structure when forming an ionic aqueous solution was equivalent in some cases to pressurizing water to 1 kbar or more (Leberman and Soper 1995).

This early x-ray study demonstrated the large gap in our understanding of what was actually going on in water at the microscopic level. Being aware of John Enderby's great enthusiasm to apply the neutron methods he had developed to the aqueous solution problem,

Table 1. The position of the main peak in the x-ray diffraction patterns from aqueous solutions of sodium chloride and nickel chloride as a function of salt concentration. The data were obtained as part of an unpublished third-year project under J Enderby's supervision in 1972 when the author was a student at Leicester University.

Salt concentration (wt %)	Momentum transfer of main peak (\AA^{-1})
Sodium chloride	
0	1.990
7	2.037
14	2.084
21	2.093
Nickel chloride	
2	1.980
4	2.021
6	2.072
8	2.062
10	1.995

I decided to stay on at Leicester and continue the study, now with neutrons and isotope substitution instead of x-rays. The rest of the story is documented by the numerous papers that have emerged. The first one, using the first-order difference method on the chloride and nickel ions, appeared in 1977 (Soper *et al* 1977). By 1990 George Neilson and coworkers had amassed a large catalogue of data on the hydration of numerous ions in aqueous solution, using the first- and sometimes the second-order difference methods, and several reviews exist (Herdman and Neilson 1990).

Meanwhile I went to Canada and the USA and worked with Peter Egelstaff and Richard Silver. The outcome of that work was that we showed how one might use H-D substitution to look at the solvent structure independently from the ions (Soper and Egelstaff 1981, Soper and Silver 1982). Nowadays more and more research groups are becoming involved in using neutrons with isotope substitution to look at the structure of water around a whole range of solutes in aqueous solution, from simple ions to large protein molecules, and there is not enough neutron beamtime to service all the demands. Neutron diffraction with isotopes is the only way of obtaining the definitive information that is needed to understand these complex systems in the liquid state. Because he was the first to tackle the aqueous solution problem head on, using the methods of neutron diffraction with isotope substitution, all this effort and activity are the direct result of John Enderby's great enthusiasm and inspiration.

In the first isotope substitution experiments on aqueous solutions we obtained, after some data analysis, the ion-water radial distribution functions. These had a few peaks at specific distances and by making sensible assumptions about which peak was due to hydrogen and which peak was due to oxygen on the water molecule we calculated the *average* orientation of the water molecule with respect to the ion. While such information is useful, it can also be misleading since there is a temptation to assume that *every* molecule around the ion adopts the average configuration. In other words it tends to reinforce the quasi-crystalline image of the liquid state which says that the surroundings of every ion are expected to look nearly the same. Moreover it may blur the distinction that the *average* configuration is not necessarily the *most probable* configuration, and it tells us nothing about the *range* of configurations which are compatible with the data. Effectively we are using the data from an elaborate tool, neutron diffraction with isotopes, to extract a very small amount of information, namely the average separation of the water molecules from the ion, and average

angle of orientation. As we probe more complex solutes in solution, it is no longer possible to make a simple interpretation of the diffraction data in terms of distances and angles—it is becoming increasingly necessary to establish the *distribution* of those quantities.

In the past few years a considerable effort has been focused on developing ways to extract a more realistic structural picture of what is going on around ions and other dissolved molecules in solution. The information obtained by experiment, typically the site–site radial distribution functions, does not yield directly the structure of the liquid. Instead these radial distribution functions are only indicators of what the true structure of the liquid, namely the four- or six-dimensional orientational pair correlation function (Gray and Gubbins 1986), might look like. Therefore the new methods of data interpretation have focused on attempting to extract this orientational pair correlation function (or parts of it), given a set of neutron diffraction data. Formally of course, such a reconstruction is impossible if the *only* information available is the site–site radial distribution functions. Therefore the only way to extract the full multi-dimensional correlation functions is to impose realistic constraints on the possible distribution functions, and I will now describe two practical methods of achieving this reconstruction.

2. Image reconstruction techniques applied to the aqueous solution problem

One of the basic assumptions of statistical physics is that real interatomic potential energy functions are continuous and have continuous derivatives, so the distribution functions of real systems are also continuous and have continuous derivatives. Therefore it makes sense to impose this continuity on any inversion of the diffraction data that is attempted. At the same time all reconstructed distribution functions are expected to be everywhere positive definite, and to satisfy certain integral conditions.

These considerations eventually led to the idea of a ‘minimum-noise’ reconstruction of the diffraction data (Soper 1990, Soper *et al* 1993) in which a quality factor for any trial distribution is calculated from its second derivative. Distributions which minimize this quality factor but which still give an acceptable fit to the diffraction data are favoured over other distributions, leading to the smoothest possible distribution function consistent with the data. The functional form of the quality factor is chosen in such a way that the ‘restoring force’ at each point in the trial distribution is independent of the height of that point away from a pre-determined baseline (Soper *et al* 1993). In this way large peaks which are implied by the diffraction data are not overly smoothed out at the expense of leaving in small features which are generated from systematic effects in the transform process. The structural damping imposed by the minimum-noise quality factor results in a smooth radial distribution function even when the supplied diffraction data are noisy.

In the case of aqueous solutions and molecular fluids the minimum-noise approach can be used to extract many of the spherical harmonic expansion coefficients of the orientational pair correlation function (Soper *et al* 1993, Soper 1994). This is because there is a direct relationship between the site–site structure factors obtained by neutron diffraction and the appropriate spherical harmonic expansion (Gray and Gubbins 1986). Although in principle the problem of solving this expansion for a given set of measured partial structure factors is highly underdetermined, application of the minimum-noise convention to these coefficients, making use of the known geometry and symmetry of the molecules involved, plus any other known restrictions on atomic overlap, greatly reduces the choice of coefficients, and permits reliable solutions in some cases, especially where the degree of orientational correlation is not too severe.

As an example of the application of this method, the spherical harmonic fit to the

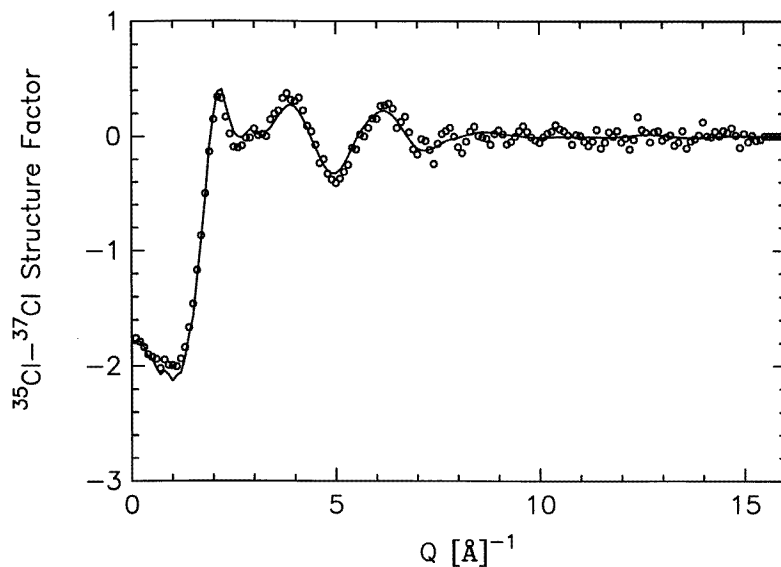


Figure 1. The first-order chlorine isotope difference (^{35}Cl - ^{37}Cl) diffraction pattern for 5.32M NaCl solutions in D_2O (circles). The line shows the spherical harmonic fit to these data using 36 coefficients.

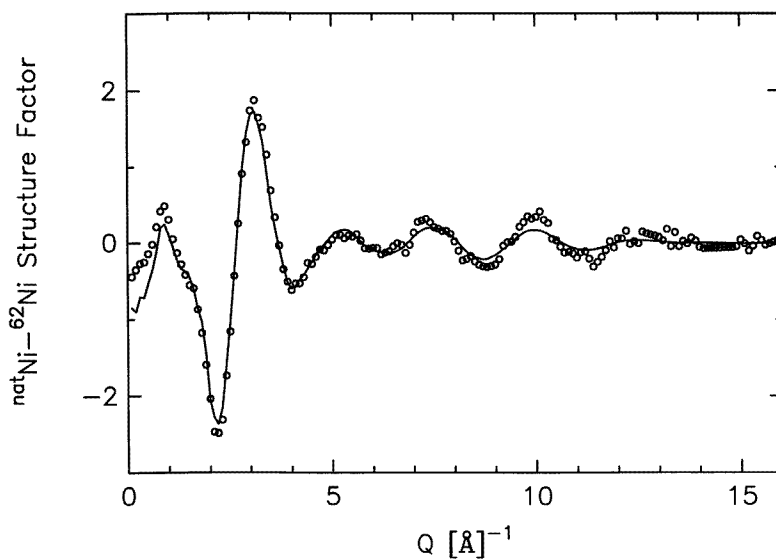


Figure 2. The first-order nickel isotope difference ($^{\text{nat}}\text{Ni}$ - ^{62}Ni) diffraction pattern for 4.41M NiCl_2 solutions in D_2O (circles). The line shows the spherical harmonic fit to these data using 36 coefficients.

first-order difference data from sodium chloride (chlorine isotope substitution) and nickel chloride data (nickel isotope substitution) from Soper *et al* (1977) is shown in figures 1 and 2. In both cases excellent fits are obtained. For the case of sodium chloride it was assumed that the water oxygen atom does not approach the chlorine ion closer than ~ 2.85 Å, while

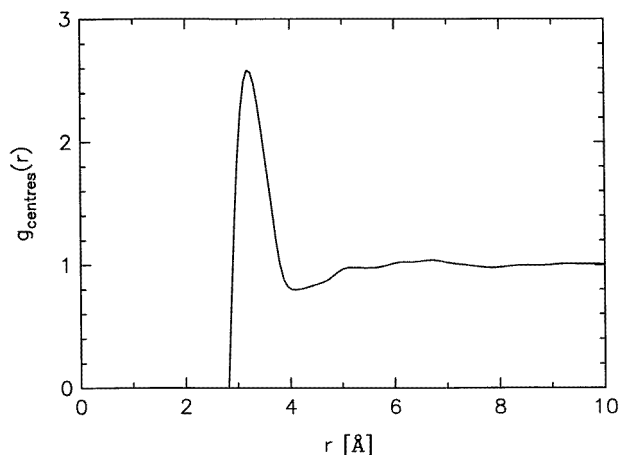


Figure 3. Estimated centre radial distribution function (Cl–water O) for water molecules around Cl^- in solution, as obtained from the spherical harmonic fit.

for the case of nickel chloride it was assumed that the water hydrogens do not approach the nickel ion closer than 2.3 Å. Both cases were analysed with 36 spherical harmonic coefficients. Figures 3 and 4 show respectively the estimated chlorine ion to water oxygen and nickel ion to water oxygen radial distribution functions as determined by this method. In both cases sharp peaks emerge, indicating a well defined first coordination shell for both ions. For the case of nickel, this peak is isolated, implying only slow exchange of water molecules with the bulk liquid, as was indicated in an earlier inelastic neutron scattering study. However in the case of chlorine the peak joins smoothly into the longer-distance region, indicating ready exchange of the hydration water molecules with the surroundings.

Figures 5 and 6 show the estimated distribution of the water molecule's dipole moment vector as a function of angle, θ , and distance, r , from each ion. In figure 5, θ is the angle which the water molecule's dipole moment makes with the chlorine ion to water oxygen (Cl–O) axis (see the inset). In this example the plane of the water molecule lies *parallel* to the Cl–O axis. θ values greater than 180° correspond to a rotation of 180° about the Cl–O axis. It is observed that pronounced peaks occur at θ values of about 130° and 230° , corresponding to an almost linear Cl–H–O bond being the most probable configuration. The fact that the early models of the data suggested the OH bond was at angle of $\sim 15^\circ$ away from linear is a consequence of the fact that diffraction data are measuring *average* distances and not the most *probable* distance, but note also that there is a $\pm 30^\circ$ spread in this angle, so that the simple idea of water molecules having a fixed geometry with respect to the ion is not valid: there is a range of orientations.

This point is reinforced for the case of the hydration of nickel ions in solution (figure 6). Here θ is the same angle as for figure 5, but now the plane of the water molecule is *perpendicular* to the Ni–O axis, so this is the case where the two hydrogen atoms on the water molecule are equidistant from the nickel ion. In this case very intense lobes are found at $\theta \approx 75^\circ$ and 285° . Note however that there is a non-trivial probability of finding orientations with the dipole moment pointing directly away from the ion, $\theta = 0^\circ$ and 360° . Information of this kind is not at all apparent from a direct Fourier transform of the data of figures 1 and 2.

A similar kind of analysis of diffraction data on methanol in aqueous solution was used to

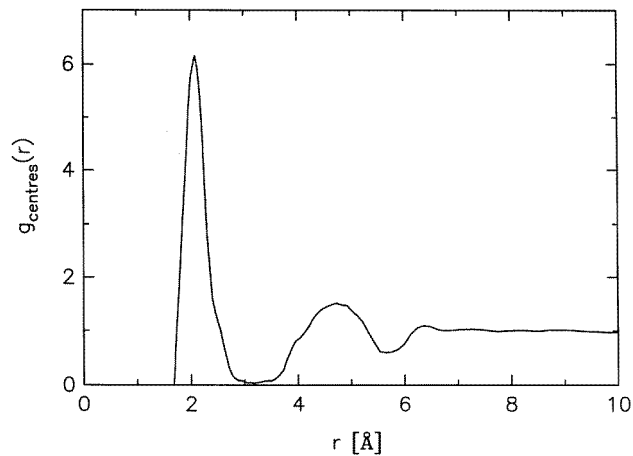


Figure 4. Estimated centre radial distribution function (Ni–water O) for water molecules around Ni^{2+} in solution, as obtained from the spherical harmonic fit.

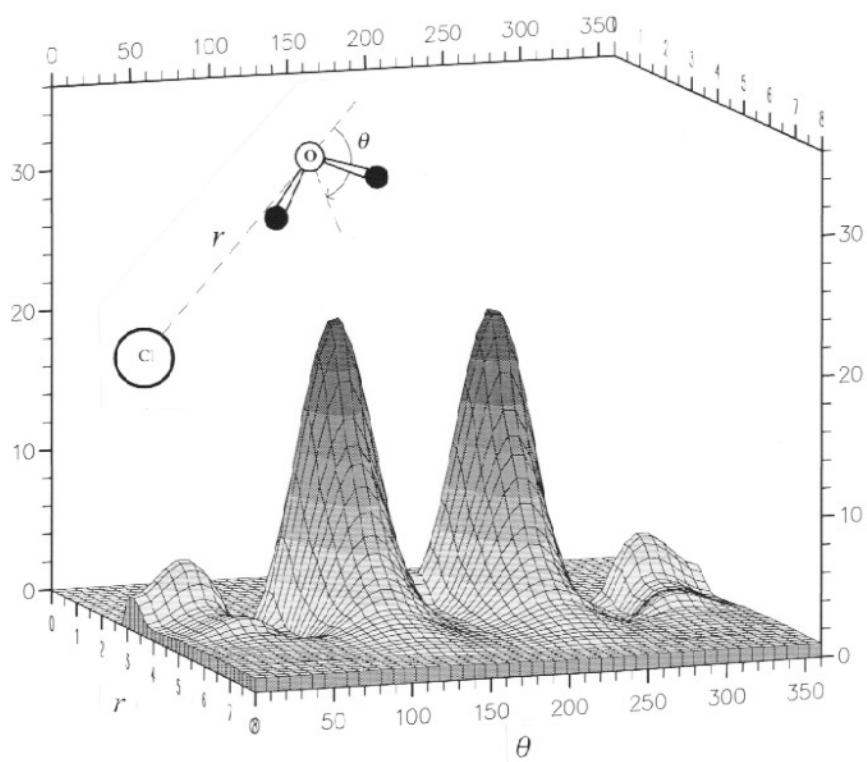


Figure 5. Probability density maps of water around the Cl^- ion in solution as a function of distance, r , from the Cl^- ion and as a function of the angle, θ , the water molecule's dipole moment vector makes with the chlorine–oxygen axis. In this plot the plane of the water molecule lies parallel to the Cl–O axis. The geometry of this plot is shown in the inset diagram.

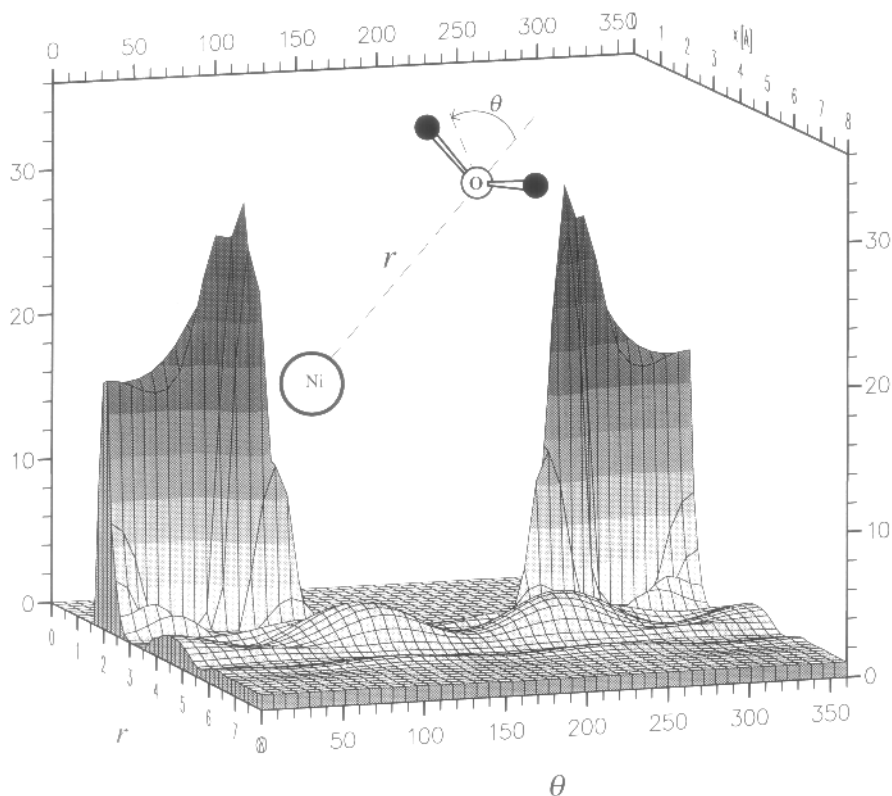


Figure 6. The same as for figure 5, but for water around the Ni^{2+} ion in solution, and in this case the plane of the water molecule lies *perpendicular* to the Ni–O axis.

demonstrate the distinctly hydrophobic nature of the hydration of this molecule in aqueous solution (Soper and Finney 1993). Clearly an enormous amount of extra information is stored in these diffraction data if only we take the trouble to extract it.

3. Empirical potential computer simulation methods

In his inaugural lecture at Leicester John Enderby made considerable reference to the important concept of ‘pseudopotential’ in the study of liquid metals. This potential effectively takes into account the screening induced by the electrons in a metal. The study of ions in solution is bedevilled by the same problem: bare ionic forces are long range and this makes computations time consuming, particularly when the standard models for the water molecules, such as SPCE (Berendsen *et al* 1987), also involve long-range forces. Recently Hummer *et al* (1994) have shown how it may be possible to use a short-ranged screened Coulombic force to study aqueous solutions without the need to invoke the time consuming Ewald summation procedure for long-range forces. Doing this would enable much larger (and therefore much more dilute) systems to be studied.

Empirical potential Monte Carlo (EPMC) simulation (Soper 1996a) was invented to circumvent situations when either the orientational correlations are strong (as in water) or when the molecular geometry is highly non-spherical: either situation requires definition of

an inordinately large number of spherical harmonic coefficients and makes their computation highly inefficient. The idea behind EPMC is similar to reverse Monte Carlo (McGreevy and Pusztai 1988) in that the object is to determine three-dimensional distributions of molecules which are consistent with the supplied diffraction data. This avoids the need to estimate large numbers of spherical harmonic coefficients. The distinction between the two methods however is that EPMC attempts to find a set of site–site interaction potentials which when used in a computer simulation of the system in question accurately reproduce the measured radial distribution functions as well as other data, such as thermodynamic data. Doing this with any of the standard potentials, such as the 6–12 Lennard-Jones potential plus charges, rarely achieves quantitative agreement. Since the radial distribution functions for a liquid are generally short ranged there is little long-range information about the interatomic potential contained in them, and as a consequence the EPMC potential is also short ranged. Therefore it too can be regarded as a kind of pseudopotential.

The EPMC method can be outlined as follows. Initially a computer simulation of the system is performed with an assumed set of site–site interaction potentials, $U_{\alpha\beta}^0(r)$. These assumed potentials can include any known features, such as repulsive-core potentials, charge distributions and molecular geometries. Once equilibrium is established in this preliminary simulation a potential of mean force can be defined for the current simulation, $\psi_{\alpha\beta}(r) = -kT \ln(g_{\alpha\beta}(r))$, while a similar potential of mean force can be derived from the radial distribution function ‘data’ derived from the diffraction experiment, $\psi_{\alpha\beta}^D(r) = -kT \ln(g_{\alpha\beta}^D(r))$. In general these two sets of potentials will not coincide so they can now be used to suggest a modification to the starting potential, $U_{\alpha\beta}^0(r)$, namely $U_{\alpha\beta}^N(r) = U_{\alpha\beta}^0(r) + (\psi_{\alpha\beta}^D(r) - \psi_{\alpha\beta}(r)) = U_{\alpha\beta}^0(r) + kT[\ln\{g_{\alpha\beta}(r)/g_{\alpha\beta}^D(r)\}]$. This new set of potentials is now used in the simulation in place of the old set, and the run continues until equilibrium is reached again. (Note there will be one site–site potential for each dataset which is available from the diffraction experiment. For those datasets where a full separation of all the individual site–site potentials is not possible by isotope substitution or other techniques, the corresponding empirical potential will be a composite potential with contributions from several site–site terms. In these cases the success of the outcome will depend much more heavily on how much prior information on atomic overlap, molecular geometry and bonding constraints is available. Providing this information can be supplied then is it likely the simulation will sample a realistic region of phase space, although further work to verify this assertion is needed.) After a suitable number of simulation steps the potential is once again modified in the same way by comparing potentials of mean force, and this whole process repeated indefinitely until a satisfactory fit to the data is obtained and the potentials of mean force coincide. At this point in the process there is now a suitable set of interatomic potentials which can be used to simulate the system in question. Practical experience with this method of refining the potential indicates that the initial refinement is extremely quick, requiring relatively few computer moves, but the final equilibrium stage when both potential and simulation are settling down can take up 12 h simulation time depending on the complexity of the system being studied.

Thus far the simulation has produced a set of molecular configurations which satisfy both the diffraction data and the known constraints on atomic overlap and molecular geometry. However it is well known that two important constraints on any simulation of a liquid are the internal energy of the simulation, and the pressure. In fact both can be controlled, within limits, in the empirical potential simulation. The energy is controlled by a simple device. Provided the expected internal energy of the system is known, and provided the internal energy of the simulation is within a reasonable range of the expected value (‘reasonable’ in

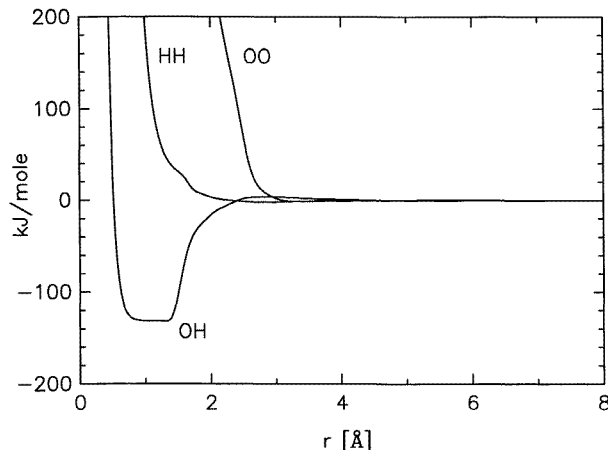


Figure 7. Empirical site-site potentials for water under ambient conditions. The magnitudes of these potentials, as well as the size and shape of the site-site repulsive components, have been constrained so that the correct internal energy and pressure are reproduced by Monte Carlo simulation with these potentials.

this instance means of the same sign, + or -, as the expected value, and with a magnitude at least 10% of what is expected) a factor F_E is applied to each iteration of the potential, $U_{\alpha\beta}^N(r) = F_E U_{\alpha\beta}^0(r) + (\psi_{\alpha\beta}^D(r) - \psi_{\alpha\beta}(r))$, with the choice of F_E dependent on the comparison between the current energy of the simulation and the expected energy. This factor has the important role of preventing the empirical potential becoming arbitrarily large or small, which it might otherwise do.

To control the pressure, use is made of the fact that the empirical potential method is weakest at low r where the radial distribution functions are most susceptible to artifacts derived from truncation errors and other systematic effects in the diffraction data. To circumvent these difficulties a set of repulsive core potentials, $U_{\alpha\beta}^{(P)}(r) = F_P \exp((1 - r/R_{\alpha\beta})/\sigma)$, is added to the empirical potential to prevent sites α and β coming too close. Here $R_{\alpha\beta}$ is a distance characteristic of this pair of sites, and σ controls the hardness of the potential. The factor F_P is adjusted up and down in the course of the simulation, depending on the actual pressure of the simulation compared to the expected pressure of the system being studied. Provided $\sigma < 1$, then the relative contribution to the pressure produced by adding this potential is much larger than the relative contribution to the energy, so the combination of F_E and F_P can be used to control the energy and pressure of the simulation. Note that, because of the iterative nature of the algorithm, the pressure is rarely controlled better than $\sim \pm 1$ kbar.

Previously (Soper 1996a) I have shown the results of applying EPMC to ambient liquid water without the control of energy and pressure. Figure 7 shows the revised empirical potentials when these controls are included. Note that at the present time these potentials are simply pixelated on a grid of radius values of separation 0.03 Å, and are not parametrized, so they could not be used as such in a molecular dynamics (MD) computer simulation. However work on developing a parametrized potential is in progress and it is hoped to apply this potential to MD in due course. Nonetheless the qualitative features of this potential are clear: it is short ranged, has an attractive O-H interaction and has repulsive H-H and O-O interactions, at low r .

4. Applications of the empirical potential method

Once a set of empirical potentials for the system is established they can be used to generate configurations of molecules, via computer simulation—indeed the configurations are obtained as part of setting up the potential—and these configurations can in turn be used to generate the spherical harmonic coefficients described in the previous section, or other structural and thermodynamic quantities. The method described in this section has been applied to a number of other systems. Some of this has been published—for example water around DMSO in solution (Soper and Luzar 1996) and pure water above and below the critical point (Soper *et al* 1996, Soper 1996b). Other work, for example on liquid hydrogen halides and on water around hydrophobic solutes in solution, is in progress. However from the point of view of the present discussion it seems appropriate to address the question of whether the empirical potential method has any consequences beyond the ability to simply generate configurations of molecules which are consistent with a given set of data. To do this the empirical potential for ambient water shown in figure 7 has been used in a series of Monte Carlo simulations of water at *non*-ambient conditions. These simulations were conducted in a constant-*NVT* ensemble, so that the density and temperature were fixed, but the energy, pressure and site–site radial distribution functions were not constrained by any data. The densities and temperatures of the simulations were chosen to coincide with those used in previous neutron diffraction experiments on non-ambient water. Table 2 lists the energies and pressures obtained in these simulations. The energy obtained with the EPMC potential along the coexistence curve at 573 K shows broad agreement with the experimental value ($-22.2 \text{ kJ mol}^{-1}$, Brodholt *et al* 1995), and the trend of increasing energy with decreasing density and increasing temperature is entirely reasonable. Within the uncertainties of the empirical potential simulation the pressures obtained are not unreasonable.

Table 2. Energy and pressure results obtained when the empirical potentials of figure 7 were used in a Monte Carlo computer simulation of water (using 256 molecules) at various densities and temperatures.

<i>T</i> (K)	ρ (mol Å ⁻³)	<i>U</i> (kJ m ⁻¹)	<i>P</i> (kbar)
298	0.033	-41.5	0.1
423	0.031	-35.8	-1.8
573	0.024	-27.0	-4.8
673	0.022	-23.3	-3.8
647	0.011	-13.1	-2.0
647	0.003	- 4.5	-0.1

Perhaps more intriguing is the comparison of the radial distribution functions obtained with this potential and those obtained from experiment. A considerable controversy followed publication of the original supercritical water data (Postorino *et al* 1993). It was alleged (Löffler *et al* 1994) that the results were affected by significant systematic errors in extracting partial structure factors from the different data. As a result the data were reanalysed (Soper *et al* 1996) but the lack of agreement between the computer simulation with the SPCE water potential model (Berendsen *et al* 1987) and the revised experimental radial distribution functions was still significant. In particular the SPCE simulation was unable to reproduce the position and height of the first intermolecular peak in $g_{OH}(r)$: the peak was too large, and at too small an *r* value, compared to the experiment.

Figure 8 compares the radial distribution function from the EPMC simulation at 573 K

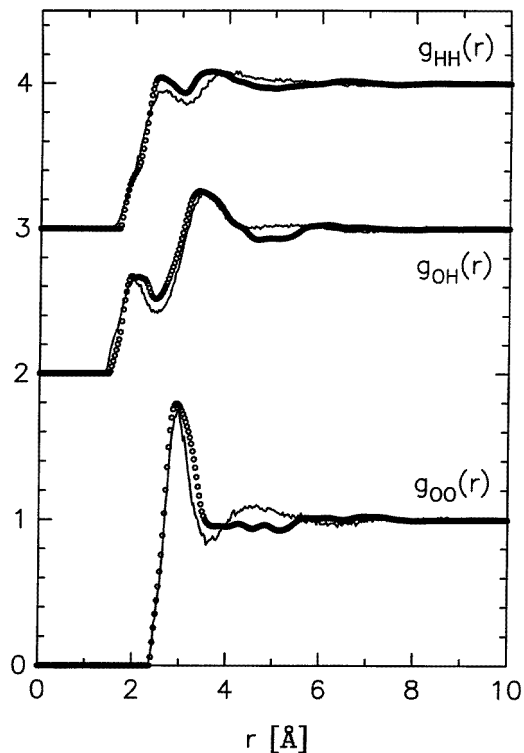


Figure 8. Estimated HH, OH and OO radial distribution functions for water at a temperature of 573 K and density of $0.024 \text{ molecules } \text{\AA}^{-3}$ (line). The circles are the results derived from neutron diffraction experiments (Soper *et al* 1996b).

with the experimental values. It can be seen that the simulated $g_{HH}(r)$ and $g_{OH}(r)$ reproduce the experimental features surprisingly accurately. Agreement with $g_{OO}(r)$ is less good—there appears to be too much emphasis of structure in the region of $r \sim 4.5 \text{ \AA}$. In fact this distribution function is the least well determined in the neutron diffraction experiment because of the significant probability of the $g_{OO}(r)$ result being contaminated by residual scattering from the substantial sample container needed for supercritical work. Other x-ray data on water in the supercritical region (Gorbaty and Kalinichev 1995) indicates that the 4.5 \AA peak is retained weakly in the supercritical region, whereas computer simulation along the coexistence curve (Guissani and Guillot 1993) suggests it will disappear completely above the critical point. The preliminary *ab initio* simulations of water in the supercritical state (Fois *et al* 1987) do not extend to this radius value with sufficient accuracy to comment on this point.

5. Discussion and conclusion

Clearly studies of the structure of water in the supercritical state (and indeed of the structure of supercritical aqueous systems) is a subject very much in its infancy. There is an overriding need for new and accurate experimental data over a range of state conditions. There is a strong need for new water potentials which reproduce the dependence of the observed distribution functions on thermodynamic state point. The empirical potential procedure

described in this paper is a potentially powerful way of obtaining an *estimate* of what the state dependence of the effective water potential might look like. When refined, the empirical potential will accurately reproduce a set of site–site radial distribution functions, so the accuracy of the potential depends only on the accuracy of the data from which it is derived. To date the empirical potential derived at ambient conditions for water already does an remarkable job of explaining the observed radial distribution functions near the critical point.

Of course it must always be emphasized that the empirical potential is only an effective potential—long-range effects will be masked unless the data themselves show long-range effects which are not the result of cooperative effects (e.g. critical fluctuations) at the temperature and density in question. This emphasizes the fact that if a full description of the water potential is one day going to be obtained it will be essential to obtain data over a wide range of thermodynamic state conditions.

In conclusion the current situation as regards the structure of water and aqueous solutions is somewhat similar to where John Enderby was when he first joined Leicester University in 1970. To quote from his inaugural lecture once more,

...It is true that the basic notion of the pseudopotential continues to be the subject of considerable theoretical scrutiny but all the experimental evidence points to its wide validity and usefulness. Initially the pseudopotential was invoked to explain the resistivity of liquid metals. Nowadays data derived from liquid metal experiments are used to estimate the strength of the pseudopotential and so the wheel has turned one full cycle in a time interval of less than ten years...

Although in the present instance the time interval is more like 25 years I believe we have now come very close to achieving the same result in water and aqueous solutions!

Acknowledgments

The work described in this paper would not have come about without the support and encouragement of numerous people, especially George Neilson, Peter Egelstaff, Richard Silver, Jacky Turner, John Finney, Alenka Luzar, Maria Antonietta Ricci, many staff members at ISIS, and of course John Enderby, who first introduced me to the aqueous solution question.

References

- Barker J A and Watts R O 1969 *Chem. Phys. Lett.* **3** 144
Berendsen H J C, Grigera J R and Straatsma T P 1987 *J. Phys. Chem.* **91** 6269
Brodholt J, Sampoli M and Vallauri R 1995 *Mol. Phys.* **86** 149
Enderby J E 1970 *Delight in Disorder* (Leicester: Leicester University Press)
Enderby J E, Howells W S and Howe R A 1973 *Chem. Phys. Lett.* **21** 109
Enderby J E, North D N and Egelstaff P A 1966 *Phil. Mag.* **14** 961
Fois E S, Sprik M and Parrinello M 1994 *Chem. Phys. Lett.* **223** 411
Gibson C 1963 *Be Your Own Weatherman* (London: Arco)
Gorbaty Yu E and Kalinichev A G 1995 *J. Phys. Chem.* **99** 5336
Gray C G and Gubbins K E 1986 *The Theory of Molecular Fluids* (Oxford: Oxford University Press)
Guissani Y and Guillot B 1993 *J. Chem. Phys.* **98** 8221
Herdman G J and Neilson G W 1990 *J. Mol. Liquids* **46** 165
Hummer G, Soumpasis D M and Neumann M 1994 *J. Phys.: Condens. Matter* **6** A141
Leberman R and Soper A K 1995 *Nature* **378** 364
Löffler G, Schreiber H and Steinhauser O 1994 *Ber. Bunsenges. Phys. Chem.* **98** 1575

- McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
- Morgan J and Warren B E 1938 *J. Chem. Phys.* **6** 666
- Narten A H and Levy H A 1969 *Science* **165** 447
- Neilson G W and Enderby J E 1983 *Proc. R. Soc. A* **390** 353
- Postorino P, Tromp R H, Ricci M A, Soper A K and Neilson G W 1993 *Nature* **366** 668
- Rahman A and Stillinger F H 1971 *J. Chem. Phys.* **55** 3336
- Soper A K 1990 *Neutron Scattering Data Analysis 1990 (Inst. Phys. Conf. Ser. 107)* ed M W Johnson (Bristol: Institute of Physics) p 57
- 1994 *J. Chem. Phys.* **101** 6888
- 1996a *Chem. Phys.* **202** 295
- 1996b *J. Phys.: Condens. Matter* **8** 9263
- Soper A K, Andreani C and Nardone M 1993 *Phys. Rev. E* **47** 2598
- Soper A K and Egelstaff P A 1981 *Mol. Phys.* **42** 399
- Soper A K and Finney J L 1993 *Phys. Rev. Lett.* **71** 4346
- Soper A K and Luzar A 1996 *J. Phys. Chem.* **100** 1357
- Soper A K, Neilson G W, Enderby J E and Howe R A 1977 *J. Phys. C.: Solid State Phys.* **10** 1793
- Soper A K, Ricci M A and Bruni F 1996 *J. Chem. Phys.* **106** 247
- Soper A K and Silver R N 1982 *Phys. Rev. Lett.* **49** 471