

Teaching Ionic Solvation Structure with a Monte Carlo Liquid Simulation Program

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The microscopic study of atoms, molecules, and their properties in an isolated state permeates almost all chemistry college textbooks (1, 2) used worldwide. Not much is discussed in these textbooks about the microscopic structure and behavior of liquids or about molecules in solution. From the quantum mechanical analysis of a single hydrogen atom to the treatment of complex molecules, the study of the physical and chemical characterization, structure, and properties of a specific atom or molecule is carried out without much further consideration of its interaction with other molecules or atoms. This approach reflects the historical development of theoretical chemistry, where simpler isolated atoms and small molecules were studied first, and, as more powerful tools were developed, it became possible to describe more complex, interacting systems. Moreover, the theoretical methods employed for the study of the structure, properties, and spectroscopy of isolated molecules have progressed markedly since the early pioneering days (3, 4). However, many systems of current interest cannot be understood if intermolecular forces are omitted. Indeed, most experiments are performed with substances in solution (5).

Several chemical reactions do not occur in gas phase and biological processes are known to occur only in aqueous environments. Real challenges are encountered in the study of systems with interacting molecules (6), such as molecular clusters and molecular liquids (3, 7). Moreover, even a cursory review of current science education publications on the subject of chemical solutions and liquids reveals that high-school students or even undergraduate students in chemistry have very little understanding of the subject. For example, some students seem not to understand the role of water in solvent-dependent reactions. In their view, water is present, but takes no active part in the reaction (8). Also, many students believe that these reactions would still take place in the absence of the solvent (9). Such mistaken notions arise from the difficulties in learning chemical representations at the macroscopic, microscopic, and symbolic levels (10).

Challenges To Understanding Solvation Structure

The failure of these students to apprehend the various levels of chemical representations seems to involve an erroneous interpretation of the meaning of the chemical representations themselves, a poor understanding of the level of description generated, and a lack of ability to shift from one representation to another when needed (11). In particular, these difficulties preclude their understanding that a typical chemical equation is but a symbolic representation of the dynamics of some complex reaction. More specifically, the students fail to realize that the use of the equation representation expresses only some specific, quantitative aspects of a

complex chemical reaction, not the whole chemical dynamical process.

On the other hand, the teaching process itself does little to alleviate the aforementioned deficiencies. In the classroom, teachers tend to favor macroscopic aspects of solution chemistry (calculation of solubility and concentration of a specific solution, macroscopic description of chemical dispersions, etc.), with little discussion of the microscopic aspects of solvation. There is also little emphasis on activities that would allow the student to easily change from one representational level to another (12).

In undergraduate textbooks (1, 2) there are basically two methodic treatments of the study of systems of atoms and molecules. The first treatment studies gases and other non-interacting or weakly interacting systems using kinetic molecular theory (KMT). These systems are studied using a statistical mechanical formulation. For example, the absence of interaction between the molecules in a perfect gas allows one to make use of statistical averaging from a microscopic viewpoint to account for macroscopic properties. Bearing in mind that each molecule or atom can be found with equal probability anywhere within the boundary of the system and using an independent-particle model, it is possible to calculate the pressure and other properties based on the microscopic properties of a single, isolated molecule (in the case of KMT, the mass of the particle). Some corrections to this idealized, noninteracting model are introduced later in the undergraduate course by virial coefficients, for example (1). Of course, statistical mechanics allows the inclusion of temperature effects in these calculations.

The second treatment of systems of atoms and molecules is the study of perfect crystals, a nonisolated state. In this topic, the long-range order (symmetry) of the crystal structure is used to describe its macroscopic structure and compute associated properties. Symmetry also allows quantum mechanical calculations of crystal electronic properties, as long as the (expectation value of the) position of each individual atom is precisely known in a particular reticle (13). Unfortunately, owing to the necessity of long-range order in the theoretical treatment, temperature effects are included only in a rather limited way.

Liquids, solutions, and liquid crystals, among other systems, present local, but not long-range order. Therefore, they have remained in a special class in which theoretical determination of their structure and properties is not straightforwardly accomplished. Indeed, on one hand particles in liquids interact much more strongly than the particles in a gas, and this prevents the use of the usual statistical mechanics methods to predict their structure and properties since the needed averaging process must be adapted to this situation. On the other hand, they are not as ordered as the atoms in a crystal

and this prohibits the quantum mechanical computing of their electronic properties using symmetry considerations. The inclusion of interaction and temperature effects, not to mention the averaging of microscopic properties of each molecule or atom in a liquid to compute its macroscopic counterparts, is needed in the modeling of liquids. Despite its current importance, both in theory and applications (5, 6), the teaching of the microscopic properties of the liquid state in undergraduate chemistry courses is limited to a simple and superficial introduction as described in physical chemistry textbooks (2).

Modeling Molecular Liquids with Computers

Nowadays, the use of computers to model the liquid state has become relatively common (3, 14, 15) and much progress has been made in the field (14). The use of molecular dynamics and Monte Carlo methods has provided efficient means to simulate the behavior of molecular liquids and solutions. In fact, it is now possible to simulate the behavior of a system with hundreds of solvent molecules on an average personal computer and thereby compute the structure and some properties of chemical solutions. In this article, we use a Monte Carlo simulation program to compute the structure of liquid water and of water as a solvent to Na^+ , Cl^- , and Ar on a personal computer, showing that it is easily feasible to use computers as an aid in teaching the behavior of liquids and solutions.

There has been much discussion about the use of computers to assist the teaching of chemistry (10, 16) and much work has been done in this area (17). Computer simulations not only allow the isolation and manipulation of individual structural and thermodynamic parameters, but also the visualization of a large set of representations (microscopic level images and animations, graphs, and numerical data) simultaneously. Such interrelated visualizations are fundamental to understanding the connections between concepts, variables, and phenomena. As an example, the use of simulations enhances the understanding of microscopic representations, a difficult problem in chemical teaching. Some controlled experiments show that students that have employed computer simulations have obtained higher scores in retention tests when compared to students that used 2- or 3-dimensional models (18). In teaching the behavior of liquids and chemical solutions, the use of computer simulations can also benefit from the fact that actual scientific research on these systems requires the use of computers. Many of these programs have been used in scientific research; therefore the simulations are accurate in the present scientific framework, as described above.

When developing simulations for teaching purposes, using scientific routines created for research purposes is a good strategy. Not only are these routines naturally based on a scientific model, their accuracy is continuously tested by simulating additional systems. Also, the teaching community may take advantage of inheriting a research simulation routine and adapting it for new teaching purposes, for further development and application of these routines. The research community can readily incorporate these adaptations in new applications of the software for the teaching community. In

this way, the simulation may become a virtual laboratory, allowing the student to explore the scientific model even beyond the initial use envisaged by the teacher. Nonetheless, care must be taken with the pedagogical context of the scientific research simulation intended to be used in teaching activities and also with limitations of the program that may lead to inaccurate results.

In this paper, we perform a simulation of the ions Na^+ and Cl^- in aqueous environment. This is perhaps the first (and sometimes the only) microscopic example of solutions discussed in chemistry textbooks (1, 2). To complement the study, we also performed a simulation of the neutral Ar atom in aqueous environment. Students tend to have, before the simulation is performed, misconceptions about the Coulombic interactions between an ionic solute and a polar solvent, and the simulation is a useful forum to address these misconceptions.

Methodology

Developing Computer Simulation Programs

In this article a set of programs that perform Monte Carlo simulations (19) of molecular liquids is used. The first of these programs is the Dice software,¹ written by Coutinho and Canuto (20), which can perform a Monte Carlo simulation of molecular liquids using Lennard-Jones plus charge potentials (21). This program has been widely used, and therefore tested, to study a number of different problems in theoretical chemistry, ranging from the analysis of the structural properties of clusters of noble gases to the generation of supermolecular liquid structures (3, 15). The second program is Dicewin,¹ written by Coutinho and Inoue (22), used to visualize the simulations performed with Dice. The pair distribution function or the graphic representation (wireframe, ball and stick, and stick only) of the simulated molecules can also be displayed with the help of Dicewin. Dicewin can be used to prepare the simulation by allowing the student to set up the thermodynamic parameters of the simulation. To set up the simulation, Lennard-Jones plus Coulomb parameters are entered for the Na^+ ion (23), followed by the SPC (simple point charge) water potential (24). This constitutes a simulation. Two more simulations were made, one of the Cl^- ion (23) in water and the other of the Ar atom (25) in water. For each species a specific set of Lennard-Jones plus Coulomb parameters was used, as described in refs 23–25. Thermodynamic variables are also set to temperature $T = 298.15$ K, the density is $\rho = 1.00$ g/cm³ (liquid water at room temperature), and the pressure is $p = 1.00$ atm. One solute (Na^+ ion, Cl^- ion, or Ar atom) surrounded by 200 molecules of water was simulated. One important issue is whether the ion–ion potential can be safely neglected at approximately the length of the box. This problem arises because periodic boundary conditions are applied in the simulation. Therefore, there are other ions placed at the center of mirror boxes around the main simulation box. The distance between these ions is the length of the box, and in the case of the simulations performed, this corresponds to a distance of approximately 18.2 Å for all simulations (Ar, Cl^- , Na^+). In the analysis performed in this article, the ion–ion potential energy can be safely neglected. The region of

interest (first solvation shell, until approximately 4 Å) is far from the other ions, and, as can be seen in Figure 1, the total potential energy between $\text{Na}^+\text{--Na}^+$ and $\text{Cl}^-\text{--Cl}^-$ at approximately 18 Å has indeed become negligible.

The total number of Monte Carlo (MC) steps was set to 2000. A step is defined as a movement or an attempt to move and rotate the entire set of molecules. In a Monte Carlo process, a movement that decreases the energy of the system is always accepted. A movement that increases the energy of the system is accepted with a probability of $e^{-\Delta V/kT}$ where ΔV is the energy variation from the initial position to the possible new position of the molecule. Therefore, the energy of the system may increase during some steps.

Running the Simulation

The initial configuration of the molecules is randomly generated. This random configuration usually has a very high energy, as molecules can be too near or too far from the other molecules, or with an orientation not corresponding to the preferential orientation of the molecules in liquid state. Therefore, to speed up the process of lowering the energy of the initial random configuration, the simulation starts by a “cooling” process of 30 steps. Unlike the Monte Carlo process itself, this “cooling” process allows only movements that decrease the energy of the system. This “cooling” process is performed to lower the initial configuration total energy to a level near the simulated liquid average energy. Here, the term “cooling” refers to lowering the total potential energy of the system under simulation, and has no intention of referring to temperature (associated with the kinetic energy of the molecules). Naturally a liquid with an average configuration possessing this energy would have to be at a high temperature. After the “cooling” process, the Monte Carlo simulation itself is performed, in 2000 steps. As explained above, the initial randomly generated configuration usually has a very high energy, and the initial “cooling” process is important to the correct computation of the average properties of the liquid. Without using the “cooling” process, it is possible to wait for the Monte Carlo process to lower the initial configuration total energy to a level near the simulated liquid average energy, but it would take more time. The fact that the initial random configuration has a high energy is an indication of an underlying specific order in the liquid system, and such an order is unveiled only after about 400 steps. An optional brief introduction to Monte Carlo simulation may be presented, including a comparison with molecular dynamics (19), depending on the background and interests of the students. Also, the instructor may discuss the effectiveness of the classical potential used for the simulation (3, 19) as compared to other more sophisticated potentials, which would make the simulation extremely slow.

While the simulation unfolds, thermodynamic and structural properties of the system can be calculated as the total potential energy and the radial distribution function (RDF), or pairwise distribution function. The RDF between the pairs of atomic species i and j is calculated by,

$$g_{ij}(r) = \frac{N_{ij}(r, r + \Delta r)}{4\pi r^2 \Delta r \rho_j} \quad (1)$$

where r is the pair distance; $N_{ij}(r, r + \Delta r)$ is the average num-

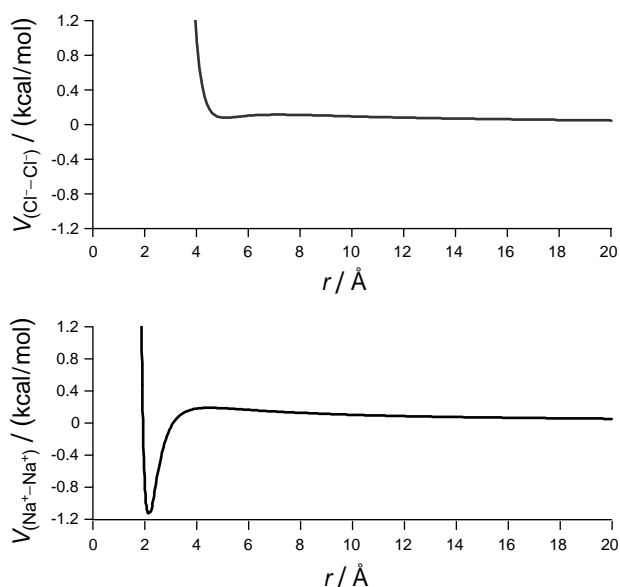


Figure 1. Total potential energy (Lennard-Jones term plus Coulomb) of $\text{Na}^+\text{--Na}^+$ and $\text{Cl}^-\text{--Cl}^-$ in kcal/mol, as a function of r .

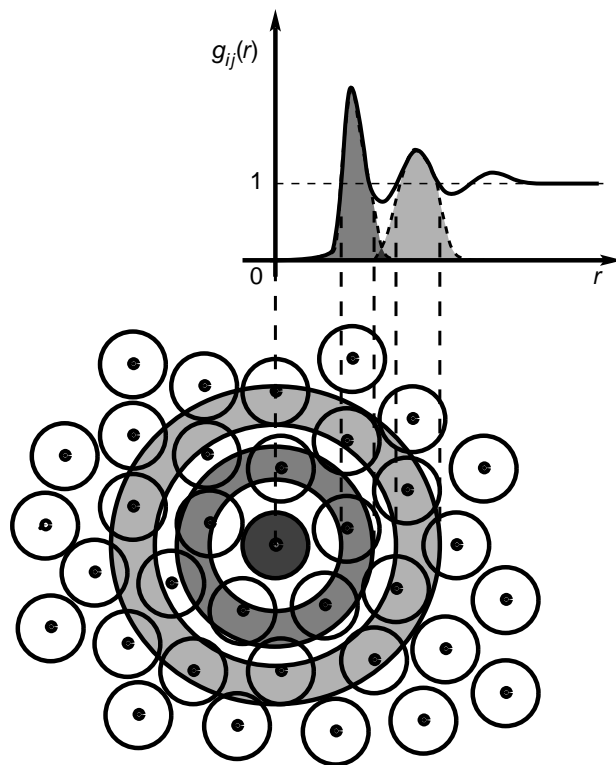


Figure 2. Schematic illustration of the computing of the radial distribution function (RDF). The peaks in $g_{ij}(r)$ indicate the distance at which the solvation shells are present. The sharper the peaks, the more organized the structure around the reference atom (reprinted with permission from ref 27).

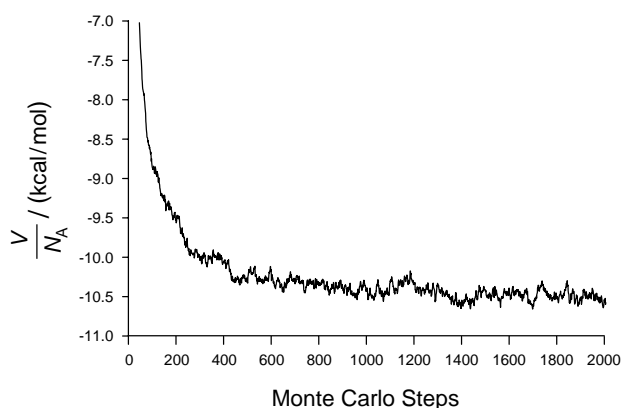


Figure 3. Average classical Lennard-Jones plus Coulomb energy of the liquid (V/N_A), in kcal/mol, as a function of the MC steps. N_A is the number of all species being simulated.

ber of atoms (of all configurations used to compute the RDF) of the species j found in a spherical shell of inner radius r and outer radius $r + \Delta r$, centered in atom i ; $4\pi r^2 \Delta r$ is the volume element of the spherical shell; and ρ_j is the number density of the species j in the simulation. The RDF, then, is the probability of finding an atom of species j at a radial distance of atom i related to the probability of finding this pair of atoms in a totally randomly distributed system with similar density. A schematic illustration of the calculation of $g_{ij}(r)$ is pictured in Figure 2. This figure shows a bi-dimensional cut of a cluster of atoms, over which the RDF, $g_{ij}(r)$, is calculated. The reference atom is located at the center of the system (dark-gray atom). The first circular shell (medium-gray) represents a section where $g_{ij}(r)$ is calculated. This circular shell contains five atom centers, thus showing a peak in the corresponding $g_{ij}(r)$, plotted above the cluster. Notice that there are no atom centers nearer to the reference atom than those within this shell. Therefore, $g_{ij}(r)$ is zero until the beginning of this first shell. Between the first shell and the second, outer shell there are two atom centers not contained by either the inner or outer shells; thus $g_{ij}(r)$ is not zero in this region. The second shell contains eight atom centers, but as the area of this shell is larger, the peak of $g_{ij}(r)$ is lower than the first shell that contains only five atom centers.

The RDFs studied in this article are calculated between the solute (Ar, Na⁺, Cl⁻) and an atom of all 200 solvent water molecules, or between solvent atoms, as between the oxygen and the hydrogen atoms. Since one hydrogen atom of a water molecule cannot be separated from the other, the two hydrogen atoms are considered as one single species. Therefore, in computing the RDF, the number density (in number of atoms per volume) of the hydrogen species (r_H) is twice the value of the water molecule number density. The number density of the oxygen species is the same as the water molecule number density, naturally.

The total number of configurations used to compute the RDF is 400 configurations. In this way, one out of five consecutive simulated configurations of the total 2000 steps (each step corresponds to a specific configuration of molecules, as described above) is saved to compute the RDF in the end. After 2000 steps, a total of 400 configurations were used to compute the RDF.

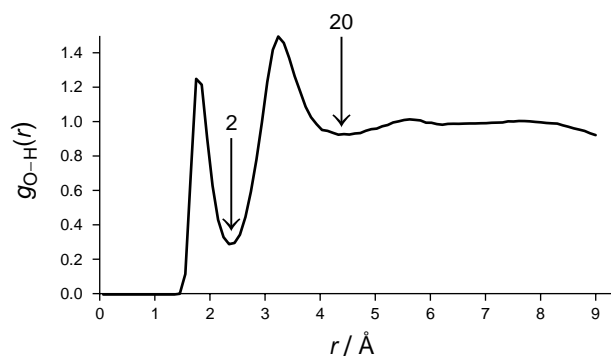


Figure 4. Radial distribution function, $g_{O-H}(r)$, of the hydrogen atoms around an oxygen atom for liquid water simulation as a function of the radial distance r (Å). The number near each arrow is the average total number of water molecules inside the indicated solvation shell.

Results

After the simulation process, it is possible to examine the total (classical) potential energy of the system as a function of the MC steps. A graph of the energy of the system versus the MC steps, as generated by the program, is shown in Figure 3. After the “cooling” process, the Monte Carlo process is performed, and the energy is naturally further lowered. The graph of Figure 3 already shows the Monte Carlo process, not showing the “cooling” process. Accordingly, the initial part of the graph shows a decreasing function as the Monte Carlo process is performed, and it is possible to notice that sometimes the energy of the system increases. The energy reaches its stabilization value of approximately (for the case of water) -10.5 kcal/mol. This stabilization energy is roughly the same for all simulations of Ar, Na⁺, and Cl⁻. As this energy is the average energy of all species in the simulation, and there is only a solute among 200 solvent water molecules, the average value of the simulation energy is basically the solvent simulation energy.

After the stabilization of the system energy, which occurs after approximately 400 MC steps, the students may proceed to the study of properties of the liquid. The teacher, comparing the high energy of the initial random configuration and the lower energy of the configuration after 400 MC steps, can initiate a discussion about the liquid structure, as described in the methodology section.

After the energy analysis, students may proceed to study the microscopic structure of the liquid. The first RDF that might be presented to the students (Figure 4) is the RDF of a water oxygen atom and the hydrogen atoms of the other water molecules, $g_{O-H}(r)$. This function shows the probability of finding hydrogen atoms around an oxygen atom as a function of the radial distance r . The corresponding graph can be obtained for each of the three different simulations, as it represents the structure of the solvent around itself. The oxygen–hydrogen pairwise distribution function, $g_{O-H}(r)$, starts around 1.5 Å (Figure 4). At this distance, as indicated by the behavior of $g_{O-H}(r)$, there is already a nonzero probability of finding water hydrogen atoms around oxygen atoms for some of the water molecules. The graph shows a sharp peak at 1.8 Å, the distance at which hydrogen bonds in liq-

uid water are usually formed. After this peak, the probability of finding hydrogen atoms decreases until approximately 2.4 Å, where the first solvation shell formed by hydrogen bonded water molecules ends. This point is indicated by the first arrow, and there is a total average number of two hydrogen atoms inside this shell, as indicated near the first arrow. After reaching this minimum, $g_{\text{O-H}}(r)$ begins to slope up again, this time forming a broader peak, at approximately 3.0 Å, indicating the formation of the second solvation shell. Such a secondary shell is typically encountered in the liquid structures of polar or nonpolar molecules. This second shell has 20 hydrogen atoms, on average. After this second shell, it is difficult to identify subsequent solvation shells, as the liquid tends not to possess any recognizable structure. Henceforth, it looks more like a gas, with atoms evenly distributed ($g_{\text{O-H}}(r) \rightarrow 1$). The same happens for the three different simulations. After a radius of approximately 8.5 Å, it is possible to notice a slight decrease of $g_{\text{O-H}}(r)$. This is an artifact of the simulation, as the simulation box is limited to approximately 18.2 Å (the maximum radius of an RDF centered in a oxygen atom in the center of this box is then 9.1 Å). Adding more water molecules would naturally solve these problems. The structure of liquid water and the nature of the specific hydrogen bonding interaction can be discussed with students. They may ask why the hydrogen bonding presents a sharper peak, while the second solvation shell presents a broader peak. This can be explained by considering the detailed nature of the hydrogen bonding interaction. Indeed, this interaction has preferred orientation and distance; molecules that do not meet these stringent geometrical attributes are therefore excluded from the first shell. Water molecules attracted by the usual dipole–dipole interaction form the subsequent shell; this interaction also has a preferred orientation, but not nearly as stringent as that of hydrogen bonding.

Before studying the other RDFs that show the solute–solvent interaction, it is important to discuss the differences among the solutes, apart from their ionic nature. One important difference is their atomic radii, as used in Monte Carlo simulation procedures. These radii are proportional to 3.4010 Å, 1.8974 Å, and 4.4172 Å for Ar, Na⁺, and Cl[−], respectively. These are the values of σ , which is the point where the Lennard-Jones potential, as a function of r , changes from a positive sign (repulsive potential), near the nuclei, to a negative sign (attractive potential). These radii will naturally act as barriers preventing water molecules from getting much nearer to the solutes. This can be seen (as discussed below) for the oxygen atoms, but not directly for the hydrogen atoms, because the oxygen atom has its own radius of 3.1650 Å, while the hydrogen atom has zero radius in the SPC water potential. The Coulombic potential modifies these values attracting the water molecules nearer to the ions, as described below.

The radial distribution functions of $g_{\text{Ar-O}}(r)$, $g_{\text{Na}^+\text{-O}}(r)$, $g_{\text{Cl}^-\text{-O}}(r)$ are shown in Figure 5. The first difference among these RDFs is the charge-bonded solvation shells presented by the ionic species, which are not present for the neutral Ar in $g_{\text{Ar-O}}(r)$. The number of oxygen atoms in the first solvation shell is also significantly different for the ionic species (6 for Na⁺ and 7 for Cl[−]) and for the Ar neutral atom (16 oxygen atoms). The charge effect is clear, since the Na⁺ ion attracts the oxygen atoms much nearer (the first peak of

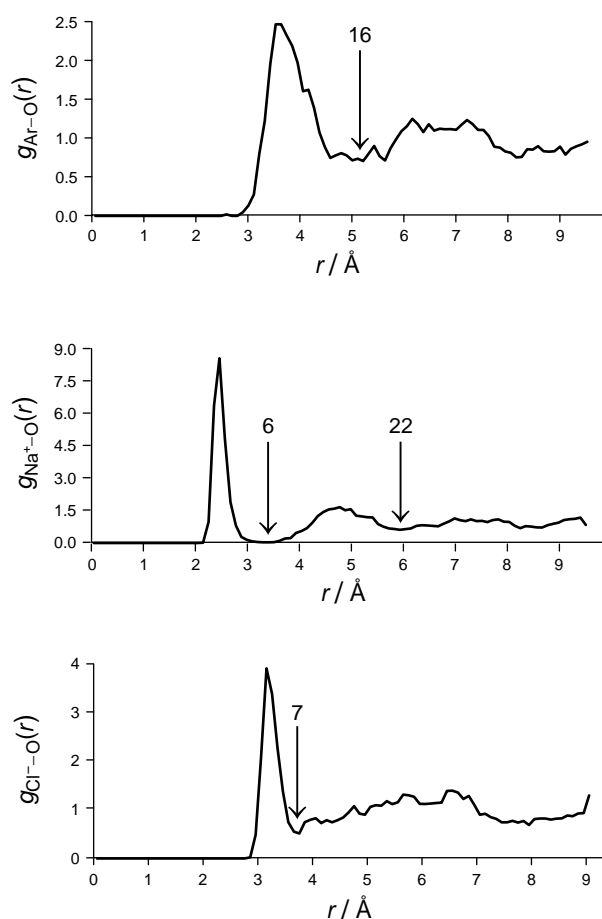


Figure 5. Radial distribution functions $g_{\text{Ar-O}}(r)$, $g_{\text{Na}^+\text{-O}}(r)$, and $g_{\text{Cl}^-\text{-O}}(r)$ of the Ar, Na⁺, and Cl[−] solutes, respectively, surrounded by the oxygen atoms of the 200 water solvent molecules as a function of the radial distance r (Å). The number near each arrow is the average total number of oxygen atoms inside the indicated solvation shell.

$g_{\text{Na}^+\text{-O}}(r)$ is at approximately $r = 2.35$ Å) than the Cl[−] ions, which naturally repel them (the first peak of $g_{\text{Cl}^-\text{-O}}(r)$ is at approximately $r = 3.15$ Å).

Another characteristic of the ionic attraction is the sharper form of the first solvation shell for both the ionic species Na⁺ and Cl[−]. This means there is a more definite structure around these species compared to the argon atom, mainly because of the charge, which forces the liquid to a specific distribution. Also, $g_{\text{Na}^+\text{-O}}(r)$ exhibits sharper and better defined peaks, compared to $g_{\text{Cl}^-\text{-O}}(r)$. This occurs because of the aforementioned attraction between the Na⁺ and the oxygen.

The $g_{\text{Ar-H}}(r)$ graph shown in Figure 6 exhibits the same behavior as the $g_{\text{Ar-O}}(r)$ graph in Figure 5, compared to the ionic species RDFs. $g_{\text{Ar-H}}(r)$ peaks at the same point as $g_{\text{Ar-O}}(r)$, at approximately $r = 3.4$ Å. $g_{\text{Ar-H}}(r)$ also displays a second, lower peak 0.2 Å before, owing to fluctuations in the simulation. Adding more steps to the simulation improves the curve, making this split peak disappear. Actually, one does not expect a split peak separated by 0.2 Å to exist, on physi-

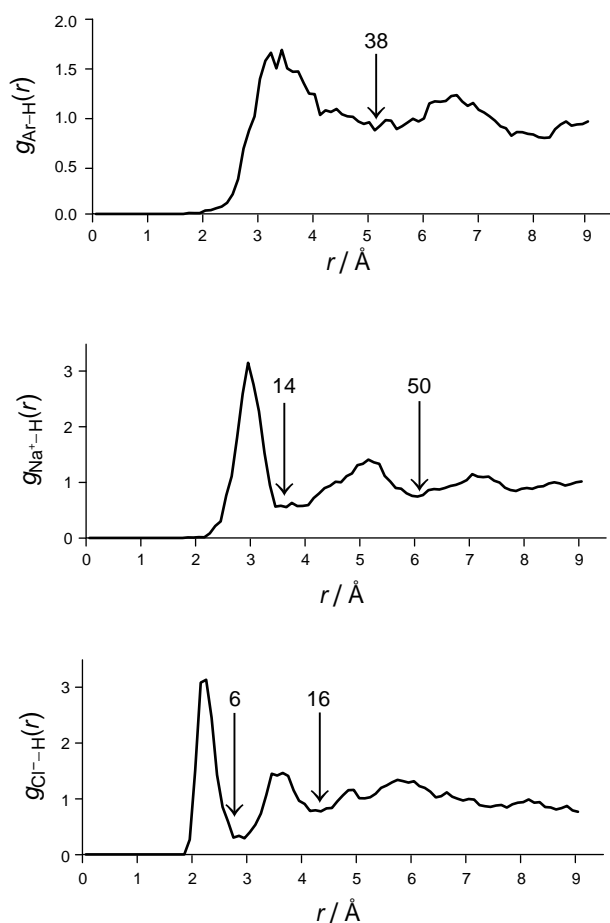


Figure 6. Radial distribution functions $g_{\text{Ar-H}}(r)$, $g_{\text{Na}^+\text{-H}}(r)$, and $g_{\text{Cl}^-\text{-H}}(r)$ of the Ar, Na^+ , and Cl^- solutes, respectively, surrounded by the hydrogen atoms of the 200 water solvent molecules as a function of the radial distance r . The number near each arrow is the average total number of hydrogen atoms inside the indicated solvation shell.

cal grounds, because 0.2 \AA is smaller than a typical bond length.

In addition, in Figure 6 the same behavior of sharpening peaks happens for the first solvation shell of the ionic species. The $g_{\text{Cl}^-\text{-H}}(r)$ RDF is likewise sharper and has a better definition than its counterpart, $g_{\text{Na}^+\text{-H}}(r)$, as a result of the direct effect of the attractive potential between the Cl^- ions and the hydrogen atoms. In fact, by comparing Figures 5 and 6, it is clear that whenever the RDF results from an attractive potential, it is more sharply defined than all other RDFs in the same figure. In Figure 6, the peaks for the RDFs occur at approximately $r = 3.45 \text{ \AA}$, 2.95 \AA , and 2.25 \AA , for $g_{\text{Ar-H}}(r)$, $g_{\text{Na}^+\text{-H}}(r)$, and $g_{\text{Cl}^-\text{-H}}(r)$, respectively. One may compare these results with the corresponding values for Figure 5 of 3.45 \AA , 2.35 \AA , and 3.15 \AA , for $g_{\text{Ar-O}}(r)$, $g_{\text{Na}^+\text{-O}}(r)$, and $g_{\text{Cl}^-\text{-O}}(r)$, respectively. It is possible to notice that, while for the argon atom no difference is perceptible between the positions of the first peaks in the hydrogen or oxygen RDFs, for the ionic species there is almost an inversion of the position of these peaks, corresponding exactly to the attractive

or repulsive nature of the specific interaction between the ion and the atoms in water. As indicated above, the net effect of the Lennard-Jones plus Coulomb potential between each ionic species and the water molecules is attractive, compared to the Lennard-Jones potential between the argon atom and the water molecules; therefore even the repelled atom of the water molecules in the first shell is nearer to the ion than the neutral argon atom.

When the difference between the first peak position for the oxygen and hydrogen RDFs in each ionic species is calculated, a value of 0.6 \AA obtains for $g_{\text{Na}^+\text{-O}}(r)$ and $g_{\text{Na}^+\text{-H}}(r)$ while the difference for $g_{\text{Cl}^-\text{-O}}(r)$ and $g_{\text{Cl}^-\text{-H}}(r)$ is 0.9 \AA . This is a consequence of the average expected orientation of the individual oxygen and hydrogen water molecules around the positive or negative ionic species. To understand this difference, the teacher can draw the water molecule geometry used in the simulation, with a hydrogen–oxygen distance of 1 \AA and the distance between the oxygen and the middle point between the hydrogen atoms of 0.58 \AA . As the natural configuration of a water molecule near the positive Na^+ has its oxygen as near as possible to the positive ion while its hydrogens are positioned symmetrically as far away as possible, this naturally leads to an average radial distance of 0.58 \AA . This value corresponds well to the distance between the oxygen and the middle point between the hydrogen atoms. That is the reason why the difference in the first peak positions for the Na^+ RDFs is 0.6 \AA . For Cl^- , the natural configuration has one of its hydrogen atoms as near as possible to the negative ion and the oxygen atom as far away as possible, corresponding to a radial distance of 1 \AA . This is also, approximately, the difference between the oxygen and the hydrogen first peaks in the Cl^- RDFs. In addition, it is important to emphasize to the students that temperature effects play a role in misaligning the water molecules, thus diminishing the expected distance of 1 \AA to the observed distance of 0.9 \AA . This misalignment is an interesting point that can be investigated by simulating the same systems with different temperatures. This point is further discussed in the conclusions.

This misalignment affects the average number of species inside each solvation shell. The average total number of oxygen atoms in the first shell, as indicated in Figure 5, is 6 for $g_{\text{Na}^+\text{-O}}(r)$ and 7 for $g_{\text{Cl}^-\text{-O}}(r)$. In the case of $g_{\text{Na}^+\text{-H}}(r)$, as indicated in Figure 6, the average total number of hydrogen atoms in the first shell is 14, but for $g_{\text{Cl}^-\text{-H}}(r)$ it is 6. To understand this difference, one must bear in mind that while there are 6 oxygen atoms in the first shell of $g_{\text{Na}^+\text{-O}}(r)$, the subsequent shell, formed by the hydrogen atoms of these first 6 water molecules, should have a total of approximately 12 hydrogen atoms. $g_{\text{Na}^+\text{-H}}(r)$ shows, in this case, an average number of 14 hydrogen atoms, a value close to the 12 hydrogen atoms expected. This shell formed by the hydrogen atoms will be, on average, at a total distance of approximately 0.6 \AA from the shell formed by the oxygen atoms. This is indicated by the difference between the position of the first peaks of $g_{\text{Na}^+\text{-O}}(r)$ and $g_{\text{Na}^+\text{-H}}(r)$ (0.6 \AA) discussed before.

In the case of the Cl^- ion, one of the two hydrogen atoms of each water molecule will approach the ion, while the single oxygen atom will be repelled, as discussed before. Therefore, in the final configuration, these hydrogen atoms form the first solvation shell for the Cl^- species, and an average of 6 hydrogen atoms, as seen in $g_{\text{Cl}^-\text{-H}}(r)$, will be present

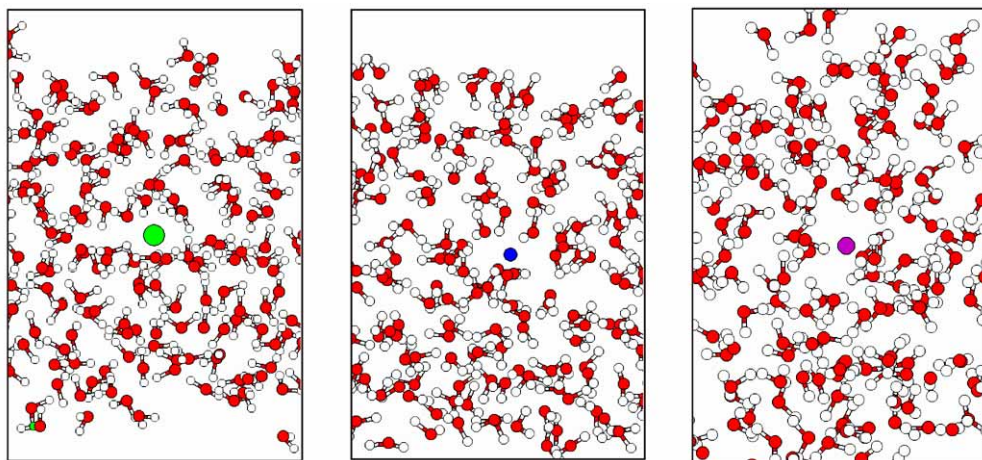


Figure 7. Visualization of the microscopic view of one sample picture generated by the simulations for Cl^- (left), Na^+ (center), and Ar (right) in water.

inside the first shell. The first shell is formed by the oxygen atoms bonded to these hydrogen atoms, and therefore a total of 6 oxygen atoms will be expected in the first shell of $g_{\text{Cl}^--\text{O}}(r)$. In fact, $g_{\text{Cl}^--\text{O}}(r)$ shows a total of 7 oxygen atoms, thus closely matching the expected value. Since the difference between the $g_{\text{Cl}^--\text{O}}(r)$ and $g_{\text{Cl}^--\text{H}}(r)$ first peaks is approximately 0.9 Å, this confirms the proposed configuration.

The atomic radii play a secondary but still important part, as can be seen by comparing the RDFs that describe the repulsive potentials $g_{\text{Na}^+-\text{H}}(r)$ and $g_{\text{Cl}^--\text{O}}(r)$. Clearly, Na^+ and H have smaller radii than Cl^- and O; therefore $g_{\text{Na}^+-\text{H}}(r)$ starts at approximately 2.3 Å, while $g_{\text{Cl}^--\text{O}}(r)$ starts at approximately 2.85 Å. The attractive potentials are described by $g_{\text{Cl}^--\text{H}}(r)$ and $g_{\text{Na}^+-\text{O}}(r)$; since these RDFs mix species with larger and smaller radii, both start at approximately 2.0 Å.

After this extensive analysis, the students can use the program to visualize the simulated systems (Figure 7). The students can manipulate each visualization (rotate, translate, and zoom in) or animate the whole set of pictures as in a movie. This allows the students to watch what is going on at a microscopic level during the simulation. Students can also choose among different graphical representations: ball-and-stick, stick-only, and wireframe representations. The students should realize that the water molecules are distributed without a specific order around the Ar atom, with the hydrogen atoms closer to the Cl^- ion, and with the oxygen atoms closer to the Na^+ ion. Students can also observe that water forms a hydrogen-bonded structure with other water molecules, especially at a large distance from the ionic species. At shorter distances, the Coulombic attraction or repulsion is the ruling factor. The competitive effect of the ion–dipole intermolecular force and the water molecule hydrogen bonding with other water molecules is a topic to be analyzed in a further article.

Preliminary results of the use of this kind of activity in a classroom show that a majority of students are able to model the molecular kinetics of substances better and they also refine their use of different chemical representations. This preliminary study involved undergraduate students in their first

general chemistry course. A final evaluation of this classroom activity has shown that after the activity, most of the students are able to model proposed macroscopic chemical phenomena based on microscopic atomic considerations (26). It is important to note that a majority of these students had never made use of a simulation of chemical phenomena before.

Conclusions

By using a Monte Carlo routine, it is possible to gain access to detailed and realistic behavior of pair distribution functions of solvated ions and neutral atoms in water. It is possible to observe, both from RDFs and from molecular visualizations, that positive ions like Na^+ attract the oxygen atoms of water molecules, while negative ions like Cl^- attract the hydrogen atoms. It is also possible to observe that water molecules near the ions prefer to orient themselves according to the ionic charge, while at a distance from the ion, the water molecules tend to align themselves according to the hydrogen-bonded structure typical of water. This presentation can be used as an introduction to solvation structural analysis.

By further exploration of Monte Carlo simulations of atoms and molecules, it is also possible to investigate the pair distribution function for gases, liquids, and solids or to investigate the evolution of these functions when the temperature of a specific material is increased, a topic that is currently being researched by our group. Increasing the temperature causes, among other variables, the misalignment of the molecules. The RDF of the solid structure would exhibit sharp peaks. By contrast, the RDF of liquids would exhibit broader peaks, indicating the small average displacement of the molecules in liquid states. Finally, the gaseous structure would exhibit little or no structure, as indicated by the RDF being a constant, since it is equally probable to find an atom in any point of the confined volume. There are some difficult points regarding these temperature effects, and we are preparing a new publication discussing the simulation of these temperature effects.

It is also possible to observe a number of different phenomena, such as cooperative effects in water solvation and hydrophobic and hydrophilic effects, among others. These phenomena can be used to understand, both qualitatively and quantitatively, the behavior of liquids as opposed to gases and solids. In addition, by having a powerful tool that allows visualization of the microscopic picture of liquids, solids, and gases, it is possible to significantly enhance teaching these microscopic concepts and representations, which usually constitute a difficult barrier in learning chemistry. One cannot overemphasize the usefulness and practicality of employing scientific, tested simulations in teaching activities, not only to explore microscopic models effectively when discussing macroscopic effects in chemical systems, but also as a computational tool that can become a virtual laboratory.

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Notes

1. These software packages are to be published and should be available soon, increasing the number of tested molecular liquid simulation software packages already in hand for use in research or teaching activities. Many other software packages (including commercial ones) can be used to reproduce the results presented here.

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