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Fluctuating Charge Force Fields for Aqueous Solutions

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Abstract

A new molecular dynamics model in which the point charges on atomic sites are allowed to fluctuate in response to the environment has been developed in a previous work (*J. Chem. Phys.*, 101:6151 (1994)). The model and its application to liquid water are briefly reviewed. Various properties of the model are calculated, with emphasis on the bonding characteristics. The water model is also used to investigate the aqueous solvation of formaldehyde.

1 Introduction

In simple molecular force fields the intramolecular electronic structure is often modeled by point charges fixed on well-defined sites in the molecular frame. The charges are constant and thus cannot respond to changing electrostatic fields which arise from movement of the atoms during the simulation. In reality, molecular electronic structure can be strongly influenced by the external environment. Charge induction effects are not pair-wise additive and improved models must go beyond pair potentials. A new simulation method in which the charges are responsive to environmental changes, presented in a recent paper[1], combines the electronegativity equalization (EE) method for determining atomic charges[2, 3, 4, 5, 6, 7] and the extended Lagrangian method for treating fictitious degrees of freedom as dynamical variables [8, 9, 10, 11]. This approach treats charges on the molecular sites as dynamical variables by introducing fictitious kinetic energy terms and self-energy terms for these charges into the Lagrangian for the system, along with Lagrange constraints ensuring electroneutrality. In this extended Lagrangian approach the charges are propagated according to Newtonian mechanics in a similar way to the atomic degrees of freedom. An application of this model to liquid water and comparisons to well-known water potentials are given in Ref. [1]. In this paper we briefly review the fluctuating charge method, and describe its application to both liquid water and a dilute aqueous solution of formaldehyde.

2 Dynamical Fluctuating Charge Models

In an isolated atom the energy of creating a partial charge, Q_A, can be expanded to second order as

$$E(Q_A) = \chi_A^0 Q_A + \frac{1}{2} J_{AA}^0 Q_A^2, \tag{2.1}$$

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where $\tilde{\chi}_A^0$ and J_{AA}^0 are parameters dependent on the atom type. The parameter $\tilde{\chi}_A^0$ is the Mulliken electronegativity of the isolated atom (per electronic charge $|e|$) and J_{AA}^0 is twice the atom's hardness. For a molecule, the polarization energy to create a set of partial charges is a sum of these atomic self-energies and intramolecular Coulomb interactions, $J_{\alpha\beta}(r)$, or

$$E_i^{\mathrm{pol}} = \sum_\alpha \tilde{\chi}_\alpha^0 Q_{i\alpha} + \frac{1}{2}\sum_\alpha \sum_\beta Q_{i\alpha} Q_{i\beta} J_{\alpha\beta}(r_{i\alpha,i\beta}) - E_i^{\mathrm{gp}}, \tag{2.2}$$

where $r_{i\alpha,i\beta}$ is $|r_{i\alpha} - r_{i\beta}|$ and E_i^{gp} is the gas-phase energy of molecule i. The total energy for N_{molec} molecules includes this polarization energy plus the usual Lennard-Jones and intermolecular Coulomb terms,

$$U(\{Q\},\{r\}) = \sum_{j<i}\sum_\alpha\sum_\beta \left(4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{i\alpha,j\beta}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{i\alpha,j\beta}}\right)^{6}\right] + Q_{i\alpha}Q_{j\beta}/r_{i\alpha,j\beta}\right) + \sum_i E_i^{\mathrm{pol}}. \tag{2.3}$$

The electronegativity per unit charge of atom A is given by $\tilde{\chi}_A = (\partial U/\partial Q_A)$. The charges, by the EE principle, are those for which the electronegativities are equal. This is equivalent to minimizing the energy subject to a charge neutrality constraint. Since the potential is quadratic in the charges, the minimization will lead to a set of coupled linear equations for the charge.

The charges are not independent variables since there is a charge conservation constraint. In the following we constrain each molecule to be neutral, $\sum_\alpha Q_{i\alpha} = 0$. We treat the charges as independent and use the method of undetermined multipliers to enforce the constraint. The Lagrangian is then

$$L = \sum_{i=1}^{N_{\mathrm{molec}}}\sum_{\alpha=1}^{N_{\mathrm{atom}}} \frac{1}{2} m_\alpha \dot{r}_{i\alpha}^2 + \sum_{i=1}^{N_{\mathrm{molec}}}\sum_{\alpha=1}^{N_{\mathrm{atom}}} \frac{1}{2} M_{i\alpha}\dot{Q}_{i\alpha}^2 - U(\{Q\},\{r\}) - \sum_{i=1}^{N_{\mathrm{molec}}} \lambda_i \sum_{\alpha=1}^{N_{\mathrm{atom}}} Q_{i\alpha}, \tag{2.4}$$

where m_α is the mass of atom α and $M_{i\alpha}$ is a fictitious charge "mass", with units of energy $\times$ time^2/charge^2, and the λ_i are Lagrange multipliers. The nuclear degrees of freedom evolve according to Newton's equation and the set of charges evolve in time according to

$$M_{i\alpha}\ddot{Q}_{i\alpha} = -\frac{\partial U(\{Q\},\{r\})}{\partial Q_{i\alpha}} - \lambda_i = -\tilde{\chi}_{i\alpha} - \lambda_i. \tag{2.5}$$

If the total charge of molecule i is a constant of the motion, then it can be shown that λ_i is the negative of the average electronegativity on molecule i. The force on the charge is simply the difference between the average electronegativity and the instantaneous electronegativity at that site.

The charge mass, $M_{i\alpha}$, a fictitious quantity, should be chosen to be small enough to guarantee that the charges readjust very rapidly to changes in the nuclear degrees of freedom[1]. The Coulomb interaction, $J_{ij}(r)$, for intramolecular pairs is taken to be the Coulomb overlap integral between Slater orbitals centered on each atomic site, with each orbital characterized by a principal quantum number, n_i, and an exponent ζ_i[6].

Table 1: Properties for potentials with the TIP4P geometry: the fixed-charge TIP4P and the flexible charge TIP4P-FQ models. Properties listed are the the gas-phase dipole moment, the dipole polarizabilities, α_{ii} (the y and z directions lie in the plane of the molecule, with the z-axis along the C_2 axis), the energy of the dimer in its minimum energy configuration, the distance between oxygen atoms for the minimum dimer configuration, and properties of the liquid as indicated.

	TIP4P[a]	TIP4P-FQ	experimental
Gas-phase dipole moment (Debye)	2.18	1.85	1.85[e]
α_{zz} (Å^3)	0	0.82	1.468±0.003[d]
α_{yy} (Å^3)	0	2.55	1.528±0.013[d]
α_{xx} (Å^3)	0	0	1.415±0.013[d]
Dimer energy (kcal/mole)	-6.3	-4.5	-5.4±0.7[e]
Dimer O-O length (Å)	2.75	2.92	2.98[e]
Liquid state properties (T=298 K, ρ=1.0 g/cm^3)			
Energy (kcal/mole)	-10.1[a]	-9.9	-9.9[a]
Pressure (kbar)	0.0[b]	-0.16±0.03	0.0
Dipole moment (Debye)	2.18	2.62	
ϵ_0	53±2[f]	79±8	78[g]
ϵ_∞	1	1.592±0.003	1.79[g]
Diffusion constant(10^{-9} m^2/s)	3.6±0.2[b]	1.9±0.1	2.30[h]
τ_{NMR} (ps)	1.4±0.2[b]	2.1±0.1	2.1[i]
τ_D (ps)	7±2[b]	8±2	8.27±0.02[j]

a) Ref. [13], b) Ref. [14], c) Ref. [15], d) Ref. [16], e) Ref. [17], f) Ref. [18], g) Ref. [19], h) Ref. [20], i) Ref. [21], j) Ref. [22]

3 Results

Pure water. The fluctuating-charge method (fluc-q) has been applied to two commonly used models of water[1], the simple point charge model (SPC)[12] and the 4-point transferable intermolecular potential model (TIP4P)[13]. Here we focus on the fluc-q version of the TIP4P model (TIP4P-FQ). Systems of 256 TIP4P-FQ or TIP4P water molecules have been simulated in the NVE ensemble at an average temperature of 298 K and a density of 1 g/cm^3, using Ewald summation for the long-ranged interactions. For more detailed discussion of the model parametrization and simulation methodology, the reader is referred to our previous work[1].

The properties of the TIP4P and TIP4P-FQ models for the water monomer, water dimer, and liquid water are listed in Table 1. The TIP4P-FQ electrostatic parameters are chosen to give the correct gas phase dipole moment for the monomer. The dimer properties listed in Table 1 are the energy of the minimum energy configuration and the oxygen-oxygen distance of this configuration. Pair potentials, such as SPC and TIP4P, are parametrized to give the experimental liquid state energies and radial distribution functions and tend to overestimate the gas phase water dimer energy. The fluctuating charge potentials predict an oxygen-oxygen separation closer to the experimental value but underestimate the dimer energy.

We have calculated both static and dynamical properties of liquid water at a temperature 298 K and a density of 1 g/cm^3. The parameters for both fluc-q models are chosen to give a binding energy of -9.9 kcal/mol. This energy includes the self polarization energy, which is the difference between the self-energy in the liquid phase and the gas phase (see Eq. 2.2). The average self-polarization energy is 5.7 kcal/mol, which represents a large contribution to the total energy.

Pair correlation functions give detailed information about the structure of the liquid. The TIP4P-FQ model gives pair correlation functions that are in good agreement with the neutron diffraction results of Soper and Phillips[23]. For details see Ref. [1]. The static dielectric constant, ϵ_0, is calculated from the fluctuations in $\boldsymbol{M}$, the total dipole of the central simulation box, by

$$\epsilon_0 = \epsilon_\infty + \left(\frac{4\pi\rho}{3kT}\right)\left[\frac{\langle M^2\rangle - \langle M\rangle^2}{N_{\mathrm{molec}}}\right]. \tag{3.1}$$

For the TIP4P-FQ model, a 1 ns simulation gave $\epsilon_0 = 79\pm8$, in good agreement with experiment. This is consistent with earlier findings that models with a dipole moment of 2.6 D have a dielectric constant near 80[24, 14, 25]. The value obtained for the optical dielectric constant, ϵ_∞, is 1.59, close to the experimental value of 1.79[19], and is underestimated because the perpendicular polarizability, α_{xx}, is zero. The frequency dependent dielectric constant, $\epsilon(\omega)$, for the TIP4P-FQ model is shown in Figure 1. The agreement with the experimental results[22, 26, 27] is very good. The close agreement in the low-frequency microwave range is due to the accurate TIP4P-FQ values of ϵ_0 and the Debye relaxation time, τ_D (the exponential decay constant for the autocorrelation function of the total system dipole, $\boldsymbol{M}$). The features at frequencies higher than 300 ps^{-1} are due to bond stretches and bends absent in the rigid geometry models used here. The highest frequency feature given by the TIP4P-FQ model is the librational mode, which shows a peak in ϵ'' at 130 ps^{-1}. The experimental peak is at 90 ps^{-1}[27]. The feature at 25 ps^{-1} has been interpreted as a translational vibration of a water molecule in its cage of nearest neighbors[28], and is not present in the spectrum for non-polarizable water models such as TIP4P[18] or Matsuoka-Clementi-Yoshimine (MCY)[29]. As argued by Neumann, this translational motion will not change the system's dipole moment much for non-polarizable models, but for polarizable models, the translational motion will induce a change in the dipole moment[18]. Therefore this feature only exists in polarizable models.

We have investigated the differences in bonding between the fluc-q and fixed-charge models by examining the distributions of pair energies, solvation energies, and residence times. In a molecular model with fixed charges, the pair energy E_{ij} is easily defined as the sum of all pairwise interactions between molecules i and j. For many-body potentials, however, there is no unique definition of a pair energy; the sum of the pair energies E_{ij} does not add up to the total system energy because the self-polarization energy is not included. There are several reasonable ways to distribute a molecule's polarization energy among the pairwise interactions in which it participates, each leading to a different definition of the pair energy. We have defined a normalized pair energy $\tilde{E}_{ij}$ by including a portion of each participating molecule's polarization energy proportional to the strength of the pair energy,

$$\tilde{E}_{ij} = E_{ij} + \frac{E_{ij}}{\sum_{k\neq i} E_{ik}}\Delta E_i^{\mathrm{pol}} + \frac{E_{ij}}{\sum_{k\neq j} E_{kj}}\Delta E_j^{\mathrm{pol}}. \tag{3.2}$$

This weighting reflects that the polarization energy varies as the magnitude of the induced dipole, and that large dipoles will be induced in pairs with strong interactions.

A distribution of pair energies is shown in Figure 2 for both TIP4P-FQ and TIP4P. The large peak centered near zero consists of the many distant, weakly interacting pairs in the liquid. The much smaller peak at low energies represents the strongly-bound close neighbors. A convenient definition of a hydrogen bond is any pair bound more strongly than the minimum in this distribution (-2.7 kcal/mol for TIP4P, -2.6 kcal/mol for TIP4P-FQ). Integrating up to this threshold gives 3.1 hydrogen bonds for both models. (Other authors have reported larger hydrogen bonding numbers, but used a different cutoff for the hydrogen bond energy[13].) The longer tail on the TIP4P-FQ distribution demonstrates the ability of fluc-q methods to allow for cooperativity in bonding; TIP4P water has a fixed lower limit of -6.2 kcal/mol on any pair interaction, while TIP4P-FQ waters have

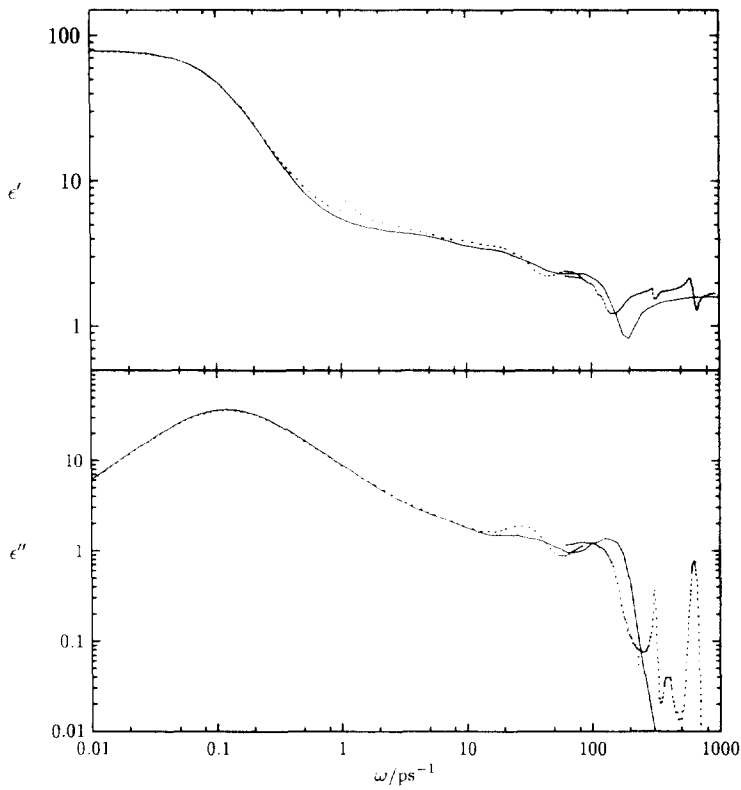

Figure 1: Real(top) and imaginary (bottom) parts of the frequency dependent dielectric constant for the TIP4P-FQ model (solid lines), compared to experiment (dotted lines).

no such restriction and can form much stronger bonds when other neighbors are oriented favorably. The average strength of a hydrogen bond for TIP4P-FQ waters is 4.38 kcal/mol, compared to 4.32 kcal/mol for TIP4P.

Cooperativity can also hinder bonding, and will generally serve to broaden the bonding distribution. Although the high-energy (weakly bound) tail of the H-bond distribution is lost in the zero-energy peak, the broadening can also be seen in the total bonding energy between one molecule and the rest of the simulation cell (obtained by summing Eq. 3.2 over a single index). The distribution of these values is centered at -20 kcal/mol for both models (twice the solvation energy per molecule) but the widths differ. The full width at half-maximum is 8.2 kcal/mol for TIP4P, and 10.1 kcal/mol for TIP4P-FQ.

Another way of examining the hydrogen bonding character of the liquid is to determine the first passage time of neighbors out of the first coordination shell, a sphere of radius equal to the first minimum in the oxygen-oxygen pair correlation function (3.3 Å for both TIP4P and TIP4P-FQ). A distribution of first-crossing times shows that the TIP4P-FQ molecules are more labile than TIP4P waters at times shorter than 0.3 ps, with a probability of escaping from the first shell increased by 8% over TIP4P waters. But at times between 0.5 and 4 ps, the TIP4P waters leave more readily, with an 18% higher escape probability. This suggests that the fluc-q waters are more fickle in forming hydrogen bonds, breaking away from unfavorable interactions more easily. But once a bond has been formed, it tends to last longer. After 4 ps, the number of molecules who have not left the first solvation shell decays exponentially, with the same decay constant for both models. A survival probability can also be defined by allowing for multiple recrossings[30], but this obscures the short-time behavior which illustrates an important difference between the two models.

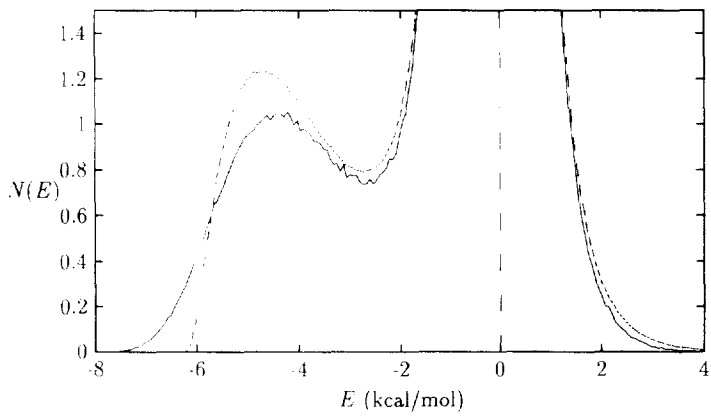

Figure 2: Pair energy distributions for TIP4P (dashed line) and TIP4P-FQ (solid line).

In general, however, the flexible charge models have slower translational and rotational timescales than the fixed-charge models, primarily due to the stronger electrostatic interactions from the higher charges. The self-diffusion constant, D, is smaller than the fixed-charge models and closer to the experimental value (see Table 1). Rotational time constants for both molecular and system dipole reorientation (τ_{NMR} and τ_D) are also slower and in good agreement with experiment.

Formaldehyde. Fluctuating charge models for water can also provide insight regarding the structural, energetic, and dynamic aspects of hydrogen bond formation between a water molecule and a solute. One expects that polarizable water molecules next to a solute molecule more polar than bulk water will have a dipole moment enhanced over the bulk value. We have studied the enhancement of the induced dipole on water molecules around a polar solute. As we will show below, the magnitude of the induced dipole on a water molecule next to a solute is strongly correlated with certain aspects of the solvation structure.

The system we studied consisted of 209 TIP4P-FQ water molecules and one formaldehyde molecule in a cubic box 18.6 Å on a side. The formaldehyde solute was based on a model of Levy and coworkers [31, 32]. The rigid, planar formaldehyde molecule has a CO bond length of 1.184 Å, a CH bond length of 1.093 Å, and an OCH angle of 122.3°. The charges on O, C, and H are -0.577, 0.331, and 0.123 $|e|$ respectively; the Lennard-Jones σ parameters are 2.85, 3.296, and 2.744 Å; and the Lennard-Jones ϵ parameters are 0.20, 0.12, and 0.01 kcal/mol. Standard combining rules were used to obtain the Lennard-Jones parameters for the interactions between formaldehyde sites and the oxygen site of TIP4P-FQ water. This model for formaldehyde yields a dipole moment of 3.9 D, which is 50% larger than the mean dipole moment of a TIP4P-FQ water molecule in bulk water. The results we present in Figure 3 are from a 20 ps run in the NVE ensemble with an average temperature of 300 K.

In the top panel of Figure 3, the mean dipole moment of a water molecule is shown as a function of the distance between the water oxygen and the formaldehyde oxygen. Waters closer than 3 Å are seen to have a dipole moment enhanced over the bulk dipole moment by as much as 0.3 D. Past 4 Å, the water dipoles rapidly approach the value of 2.62 D characteristic of the bulk liquid. It is interesting to note the dip in the dipole moment of water molecules about 3 Å away from the formaldehyde molecule. Waters in this region are caught between the first and second solvation shell. These water molecules presumably lack the opportunity to form a strong hydrogen bond with either the formaldehyde or a neighboring water molecule. Consequently a smaller dipole moment is induced on these water molecules than the mean dipole induced on bulk water.

The bottom panel of Figure 3 shows the strong angular correlations exhibited by water molecules between the first and second solvation shells. The cosine of the OHO angle formed by the formaldehyde oxygen and the HO of a water molecule is nearly 1 for water molecules closer than 3 Å, indicative of a strong linear hydrogen bond. There is a precipitous drop at 3 Å, signaling the breaking of the hydrogen bond as the water molecule leaves the first solvation shell. Other angular correlations do not show nearly as sharp a jump between the first and second solvation shells. The dashed line, for instance, depicts the cosine of the angle made by the formaldehyde CO and a water oxygen. This angle tends to be more linear for waters closer to the formaldehyde, and angular correlation is lost slowly as the water moves away. The cosine of the angle between the symmetry axes of formaldehyde and water is shown in the dotted line. This angular correlation is also weak compared with the dramatic behavior of the OHO angle.

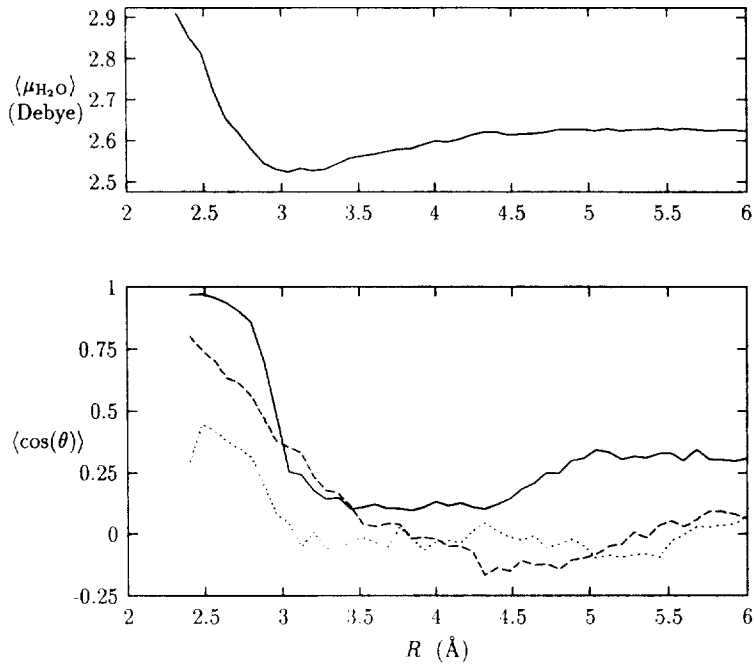

Figure 3: Dipole moments of TIP4P-FQ water molecules are shown with angular correlations with a formaldehyde solute.
Top panel: The average dipole moment $\langle\mu\rangle$ of fluctuating charge water molecules is shown as a function of R_{OO}, the distance from the water oxygen to the formaldehyde oxygen.
Bottom panel: $\langle\cos(\theta)\rangle$ for three different angles made between CH_2O and H_2O as a function of R_{OO}. Solid line: θ = O − HO angle for the H on H_2O closer to the O on CH_2O; Dashed line: θ = CO − O angle; Dotted line: θ = the angle between the C_{2v} axes of CH_2O (taken from C to O) and H_2O (taken from the HH midpoint to O).

4 Conclusion

The fluctuating charge model, as applied to liquid water, was shown to be an effective method for treating polarization effects. The fluc-q method introduces no intermolecular interactions beyond those already present in fixed-charge models, and the propagation of the charges using extended Lagrangian methods increases the computational cost by only a modest amount (about 10%). In contrast, other methods which include polarizability to dipolar order introduce an additional interaction (the dipole-dipole interaction) which, together with solving for the induced dipole moments,

increases the CPU time by about a factor of 2 over fixed charge models[33, 34]. The electronic properties of the fluc-q water model are such that in the gas phase it gives the correct dipole moment and in the liquid phase the dielectric properties are well reproduced for a range of frequencies (see Figure 1). In addition, the fluc-q model gives good estimates for the liquid-state radial distribution functions and dynamical properties such as the diffusion constant and τ_{NMR} (see Table 1). In comparison to fixed-charge models, average bonding properties appear to be no different under the fluctuating-charge model, but the charge flexibility and many-body character of the potential both help to broaden the distribution of bonding energies and encourage cooperative bonding behavior. In studies of formaldehyde solvation, we detect a strong correlation between the dipole induced on a water molecule and the presence of a linear hydrogen bond between the water and the solute.

We are conducting ongoing studies of solvation dynamics to further characterize the relationship between electronic polarization, solvation structure, and solvation energetics. Other current work includes studies of the solvation of ions, using a Drude dispersion oscillator to model the ion polarizability, and of small organic molecules, examining the coupling of the molecular charge distribution to torsional bond rotation, to functional group substitution, and to the aqueous environment.

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