



Dipolar Correlations and the Dielectric Permittivity of Water

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(Received 17 March 2007; published 13 June 2007)

The static dielectric properties of liquid and solid water are investigated within linear response theory in the context of *ab initio* molecular dynamics. Using maximally localized Wannier functions to treat the macroscopic polarization we formulate a first-principles, parameter-free, generalization of Kirkwood's phenomenological theory. Our calculated static permittivity is in good agreement with experiment. Two effects of the hydrogen bonds, i.e., a significant increase of the average local moment and a local alignment of the molecular dipoles, contribute in almost equal measure to the unusually large dielectric constant of water.

DOI: 10.1103/PhysRevLett.98.247401

PACS numbers: 78.30.Cp, 32.10.Dk, 61.25.Em

The large dielectric constant of water, $\epsilon_0 \sim 78$ at room temperature (RT), contributes to make it the most important polar solvent in chemistry and biology. The dielectric constant of water is higher than that of all other polar liquids made of molecules with a comparable dipole moment. This behavior can be associated to the presence of an underlying hydrogen-bond (H-bond) network [1]. Crystal-line water structures with an intact H-bond network, such as ice Ih, exhibit even larger dielectric constants ($\epsilon_0 = 96.5$ at the freezing temperature). Yet a detailed understanding of the dielectric properties of water and ice, based on first-principles microscopic theory, is still missing.

In the linear response regime the dielectric constant is related to the fluctuation of the dipole moment of a macroscopic sample. Assuming periodic boundary conditions, the linear response relation takes the form [2,3]

$$\epsilon_0 = 1 + \frac{4\pi}{3} \frac{\langle \vec{M}^2 \rangle}{Vk_B T}, \quad (1)$$

where \vec{M} is the dipole moment, V is the volume, and T is the temperature. If the dipole \vec{M} is given by a sum of N molecular moments $\vec{\mu}$, we may write

$$\langle \vec{M}^2 \rangle = N\mu^2 \left(1 + \sum_i N_i \langle \cos\theta_i \rangle \right) = N\mu^2 G_K. \quad (2)$$

Here the sum extends to the coordination shells of a tagged molecule, N_i is the number of molecules in the i th coordination shell, $\langle \cos\theta_i \rangle$ is the average cosine of the angle between a dipole in the i th coordination shell and the dipole of the central molecule. This expression defines the correlation factor G_K , which accounts for angular correlations among the dipoles [4]. G_K depends on the boundary conditions (see, e.g., Refs. [2,3,5,6]) due to the long range of the electrostatic interactions [7].

For uncorrelated dipoles $G_K = 1$. In water and ice, H bonds forbid configurations in which the dipoles of adjacent molecules point in opposite directions, originat-

ing a local alignment of the dipoles [10]. As a consequence the value of G_K is greater than 1. In addition H bonds pull further away positive and negative charges within a molecule, enhancing the average molecular moment in condensed phases.

Within the above phenomenological theory μ and G_K are independent empirical parameters. Unfortunately, individual molecular moments in water and ice are not experimentally accessible, reflecting a basic arbitrariness in partitioning the electronic charge between individual molecules in a condensed environment [11,12]. In this context, experimental estimates such as $\mu = 2.9 \pm 0.6$ D based on the measured x-ray form factor of liquid water [13], or theoretical estimates based on various partitioning schemes [14–16], should be taken mainly as indicative values.

Predicting the dielectric constant of water has long been a challenge for theory. In a pioneering paper, Pople [17] adapted Kirkwood's theory [8] to water by postulating that the main effect of liquid disorder was to bend the H bonds but otherwise fourfold ice coordination was preserved. By adopting a distribution of the bending angles to fit the experimental pair-correlation function, he estimated the correlation factor g_K [7] to be ~ 2.5 at RT. Then, estimating that μ in the liquid was about 16% larger than the experimental gas phase value ($\mu_{\text{gas}} = 1.85$ D), he obtained a RT dielectric constant of ~ 64 , in fairly good agreement with experiment ($\epsilon_0 \sim 78$). This agreement was, however, partly fortuitous, as long range electrostatic effects were neglected (see, e.g., Ref. [2]).

More recently the dielectric constant of water has been studied with molecular dynamics simulations that permit arbitrary distortions of the H bonds without requiring that fourfold coordination be preserved. These simulations are based on empirical models that usually reproduce well the experimental pair-correlation function and other properties of the liquid. Unfortunately this does not unambiguously fix the dielectric properties as illustrated by a recent study

of several popular water models [18], which reports values of μ ranging from 2.27 to 2.82 D, and values of the reaction-field g_K [7], ranging from 2.57 to 5.13. Not surprisingly, the corresponding RT permittivity ranges from ~ 65 to ~ 171 .

The key point is that the values of μ and of the correlation factor reflect the unique electronic and molecular structure of the liquid. To address this issue we investigate the static dielectric properties of water from the point of view of *ab initio* molecular dynamics (AIMD). In this approach a liquid is regarded as a collection of nuclei and electrons. Molecular structure and dielectric polarization derive consistently from the quantum mechanical ground state of the electrons within density-functional theory (DFT). In spite of the ambiguity in the definition of the local moments in condensed phase, it is convenient to associate dipoles to individual molecules [12,16] in terms of maximally localized Wannier functions (MLWF) [19]. The cell dipole is given by the sum of the molecular moments in a cell. The advantage of this formulation is that, while the molecular moment is itself not a physical observable [20], its derivatives or fluctuations are well-defined physical observables that describe the response of the system to a macroscopic electric field [11,12].

The above approach leads to a meaningful microscopic definition of the parameters μ and G_K . By applying this scheme to water, we calculate a dielectric constant that, within current theoretical and computational limitations, is in excellent agreement with experiment.

We simulate the liquid with a modified Car-Parrinello (CP) scheme [21,22], in which MLWFs [19] are used in place of delocalized Bloch orbitals to represent “on the fly” the electronic wave functions. Our sample is a periodically repeated cubic cell containing 64D₂O molecules at a temperature of ~ 330 K and a density of 1 g/cc in the canonical ensemble. The choice of heavy water is motivated by reasons of computational efficiency [16]. With our choice of parameters [23], the structural and dynamical properties of the simulated liquid reproduce well the corresponding experimental properties. In particular, our simulated liquid shows diffusive behavior during an AIMD trajectory lasting for 20 ps after 2 ps of equilibration. The calculated diffusion coefficient is $D = 1.6 \times 10^{-5}$ cm²/s, compared to an experimental value of $D = 1.86 \times 10^{-5}$ cm²/s for D₂O at RT.

The diffusive character of liquid water in AIMD runs is highly sensitive to the parameters of the simulation [27]. Typically AIMD water exhibits sluggish diffusion at RT. The glassy behavior is more pronounced for large plane-wave cutoffs, i.e., for a better converged electronic structure, and for small values of the fictitious electronic mass parameter in the CP equations, i.e., for a more accurate Born-Oppenheimer evolution. The sluggish behavior persists up to temperatures ~ 50 – 100 K above the freezing point, depending on the parameters of the simulation. Likely, this behavior indicates a tendency of current DFT functionals to overestimate the H-bond strength [28].

However, an overestimate of the H-bond strength of the order of 100 K, i.e., 0.01 eV, is small on the scale of the H-bond energies (~ 0.2 eV in water) and should not affect significantly the main features of a simulation when the sample is diffusive. In this respect our choice of parameters is a compromise that gives a reasonably good liquid at 330 K for times of the order of 20 ps.

As in Refs. [12,16] we assign a dipole $\vec{\mu}_i = \vec{r}_{D_1}^i + \vec{r}_{D_2}^i + 6\vec{r}_O^i - 2\sum_{\ell=1,4}\vec{r}_{W_\ell}^i$ to the i th molecule in the cell, where \vec{r}_X^i are the positions of the two deuterons ($X = D_1, D_2$), of the oxygen nucleus ($X = O$), and of the four MLWF centers ($X = W_\ell$ with $\ell = 1, 4$) associated to the eight valence electrons of the molecule. The i th dipole is conventionally located at the molecular center of mass \vec{r}_i , and depends on the local environment. We define the dipolar density $\vec{m}(\vec{r}) = \sum_{i=1,N}\vec{\mu}_i\delta(\vec{r} - \vec{r}_i)$ and its correlation function $C_m(r)$,

$$C_m(r) = \frac{1}{N} \int d\vec{r}' \langle \vec{m}(\vec{r} + \vec{r}') \cdot \vec{m}(\vec{r}') \rangle \\ = \frac{1}{N} \left\langle \sum_{i \neq j} \vec{\mu}_i \cdot \vec{\mu}_j \delta(\vec{r} + \vec{r}_i - \vec{r}_j) \right\rangle + \langle \vec{\mu}^2 \rangle \delta(\vec{r}), \quad (3)$$

where we take advantage of the macroscopic homogeneity and isotropy of a liquid. We then define the dipole pair-correlation function $\rho c_m(r) = C_m(r) - \langle \vec{\mu}^2 \rangle \delta(\vec{r})$, where ρ is the molecular number density.

The calculated dipole pair-correlation function $c_m(r)$ is reported in Fig. 1. We also report in the same figure the oxygen-oxygen pair-correlation function $g_{OO}(r)$, obtained in the same run, superimposed to an experimental $g_{OO}(r)$ at RT from neutron diffraction data [29].

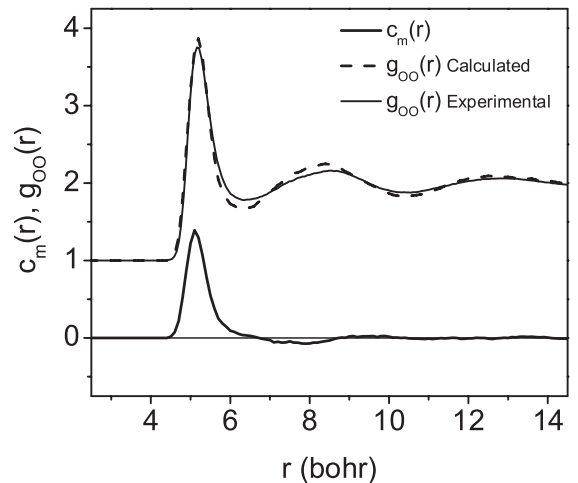


FIG. 1. Calculated dipole pair-correlation function $c_m(r)$ (wide, solid line), calculated (dashed line), and experimental (thin line) partial pair-correlation function $g_{OO}(r)$. The cubic simulation box has an edge $a = 23.464$ bohr. Correlations up to distances larger than $a/2$ are included by appropriately normalizing the correlations between the central molecule and the molecules near the corners of the simulation box.

The strong positive dipolar correlation in the first coordination shell reflects the alignment of adjacent dipoles generated by H bonds. A small antialignment is present in correspondence of the second peak of the pair-correlation function, whereas an almost imperceptible positive alignment appears at larger distances. The persistence of dipolar correlations up to intermediate range reflects the associated nature of the liquid. The small magnitude of the dipolar correlations beyond the second coordination shell suggests that the dipole correlation length λ_m should not be significantly larger than the accessible range of distances in our simulation.

The integral of Eq. (3) over all space gives the fluctuation of the macroscopic moment $\langle \vec{M}^2 \rangle = N \int d\vec{r} C_m(r)$. Thus the average fluctuation of the cell dipole in Eq. (1) can be expressed in terms of the radial integral of $C_m(r)$ or, equivalently, in terms of the radial integral of the dipole pair-correlation function $c_m(r)$, if the range of integration extends to distances larger than λ_m . Then the correlation factor G_K can be defined as follows

$$\langle \vec{M}^2 \rangle = N \langle \vec{\mu}^2 \rangle G_K = N [\langle \vec{\mu}^2 \rangle + \rho \int d\vec{r} c_m(r)]. \quad (4)$$

In Fig. 2 we show $G_K(R)$, i.e., the computed correlation factor G_K when the radial integral extends up to a radius R in Eq. (4). In our simulation spanning 20 ps, $G_K(R)$ is well converged up to distances of ~ 12 bohr, while larger error bars affect the integrated dipolar correlation at larger distances where small fluctuations in $c_m(r)$ get amplified by the volume integral in Eq. (4). Larger simulation times and/or boxes would reduce these errors.

From Fig. 2 we extract $G_K = 2.2 \pm 0.2$. The most important contribution (~ 2.06) comes from the first shell of neighbors. This is close to the first neighbors contribution

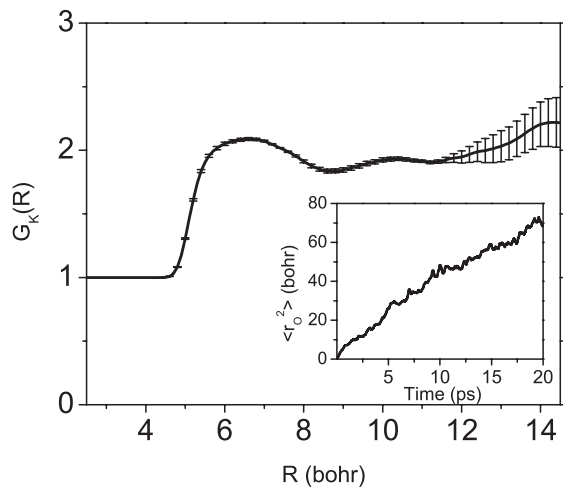


FIG. 2. $G_K(R)$ from a 20 ps trajectory. The error bars are estimated from the block average fluctuation calculated by dividing the trajectory into 5 blocks of 16 ps each. Each subsequent block starts 1 ps after the beginning of the preceding one. The inset shows the mean square displacement of the oxygen atoms.

(~ 2.33 [30]) that one would obtain for a disordered distribution of the H bonds consistent with the Bernal-Fowler rules [10]. Considering that in our sample ~ 15 percent of the H bonds are broken on average, we conclude that in *ab initio* liquid water entropic effects play a major role in the distribution of the relative molecular orientations at short range.

We report in Fig. 3 the simulated distribution of molecular dipoles, yielding $\mu \equiv \sqrt{\langle \vec{\mu}^2 \rangle} = 3.09$ D; the distribution is very similar to the one previously reported by Silvestrelli and Parrinello [16]. The molecular moments in the liquid are considerably larger than our calculated gas phase value of 1.87 D. The magnitude of the effect signals that local tetrahedral coordination is well preserved in the liquid. Our μ value is in the range suggested by measurements of the x-ray scattering form factor [13]. Moreover, it coincides with the value used in a recently proposed improved empirical model potential of water that includes diffuse charges [31]. This model leads to a dielectric constant in excellent agreement with experiment at all liquid state points. The dielectric constant, Eqs. (1) and (4), depends on the product $\langle \vec{\mu}^2 \rangle G_K$: both terms are responsible for its high value.

Our first-principles computed value at 330 K is $\epsilon_0 = 67 \pm 6$, in agreement with the experimental value $\epsilon_0 = 68$ at the same temperature [32,33]. In making this comparison, we are disregarding an issue that is numerically irrelevant, though important as a matter of principle. In fact, we are using the *classical* fluctuation formula, Eq. (1), while the $T = 0$ electronic response ϵ_∞ obeys a different (quantum) fluctuation formula. The error is nonetheless very small ($\epsilon_\infty - 1 = 0.8$ in water).

The above approach can also be applied to ice. The experimental dielectric constant of ice Ih at the melting point is 96.5, i.e., about 9% higher than the dielectric constant of the coexisting liquid phase (87.9). Thus the

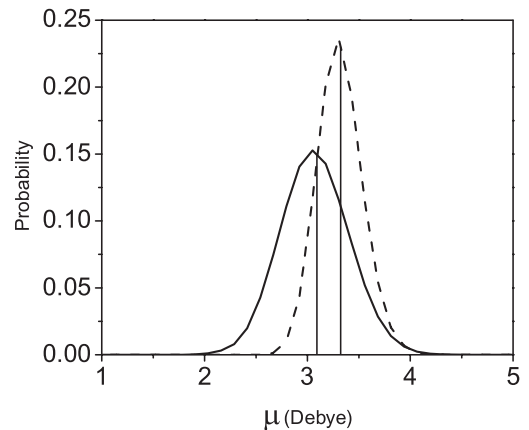


FIG. 3. Distribution of the molecular dipoles from an AIMD run at $T = 330$ K. The vertical thin line indicates $\mu \equiv \sqrt{\langle \vec{\mu}^2 \rangle}$. Also shown (dashed line) is the distribution of molecular dipoles and the corresponding μ from a AIMD run for Ih ice at $T = 273$ K.

product $\langle \vec{\mu}^2 \rangle G_K$ should increase by 16% upon freezing to compensate for the corresponding 8% increase of the specific volume. Performing the large number of electronic structure calculations needed to sample proton disordered configurations in ice would be prohibitively expensive, preventing us from calculating G_K . We can, however, easily calculate the molecular moment distribution corresponding to a single proton disordered configuration. Since molecular moments depend essentially only on the local environment of each molecule, the distribution corresponding to a single proton disordered configuration is statistically representative. In this calculation we use a periodic cell with 96 molecules arranged in the ice *Ih* structure at the experimental density. We generate proton disordered configurations with the Rahman-Stillinger algorithm [34]. Eventually, one of these configurations is used to start an AIMD run at 273 K. The moment distribution from this run is reported in Fig. 3: it has $\mu = 3.32$. This implies that G_K should be ~ 2.55 for the dielectric permittivity to agree with experiment. Interestingly, this value of G_K for ice agrees well with the predictions of simplified statistical mechanical models that include dipole-dipole interactions [35].

In conclusion, our analysis shows that the dielectric response of water and ice is dominated by the short range effects of the H bonds. Local tetrahedral coordination is responsible for an average local moment in excess of ~ 3 D. Local tetrahedral coordination and the ice rules [10] further contribute to a correlation factor larger than 2. The dominating role of short range effects implies that even minuscule quantities of water, as one can find in nanoconfined geometries such as in protein pockets, should be capable of substantial dielectric screening [36].

Work partially supported by the NSF through Grant No. CHE021432 and by ONR through Grant No. N00014-01-0570.

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