

Structure of the floating water bridge and water in an electric field

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The floating water bridge phenomenon is a freestanding rope-shaped connection of pure liquid water, formed under the influence of a high potential difference (approximately 15 kV). Several recent spectroscopic, optical, and neutron scattering studies have suggested that the origin of the bridge is associated with the formation of anisotropic chains of water molecules in the liquid. In this work, high energy X-ray diffraction experiments have been performed on a series of floating water bridges as a function of applied voltage, bridge length, and position within the bridge. The two-dimensional X-ray scattering data showed no direction-dependence, indicating that the bulk water molecules do not exhibit any significant preferred orientation along the electric field. The only structural changes observed were those due to heating, and these effects were found to be the same as for bulk water. These X-ray scattering measurements are supported by molecular dynamics (MD) simulations which were performed under electric fields of 10^6 V/m and 10^9 V/m. Directional structure factor calculations were made from these simulations parallel and perpendicular to the E-field. The 10^6 V/m model showed no significant directional-dependence (anisotropy) in the structure factors. The 10^9 V/m model however, contained molecules aligned by the E-field, and had significant structural anisotropy.

water electric field | pair distribution function | temperature dependence | high voltage

It is well known that a stream of water can be deviated by the static electricity on a plastic rod (1) and this has often been explained by the water molecules being “partially aligned in the electric field” (2). The arrangement of water molecules in electric fields and at charged surfaces has important implications in electrochemistry, mineralogy, and biology (3–5). Hydrogen bonding is weakened perpendicular to very high electric fields (approximately 10^9 V/m), and strengthened along the direction of the field. This modification of the hydrogen bonding is due to partial alignment of the water molecules, and affects the existing three-dimensional network in an anisotropic manner. In weaker electric fields a striking visual illustration of the effect of high voltage applied to pure water is the formation of a stable thread, a few millimeters in diameter between two beakers, known as the floating water bridge (6). Under these conditions, electric fields of approximately 10^6 V/m enable the free standing bridge to facilitate water flow from one beaker to another over a distance of up to approximately 25 mm (the field strength estimate is calculated from the applied voltage divided by the bridge length). This water bridge phenomenon is essentially an extension of the Taylor cone, and cone-jet formations which are responsible for electrosprays. A Taylor cone, first explained in 1964 (7), is the formation of a cone shaped liquid surface due to high electric fields, which at higher field strength deforms further to emit a jet. This cone-jet phenomenon is understood in terms of the surface charge deforming the liquid toward a surface of equal electrical potential.

Recent measurements however, have suggested that there is also preferred orientation of water molecules along the electric field within the floating water bridge (6, 8–14). If correct, this

preferred orientation has broader implications for the behavior of water under these relatively modest approximately 10^6 V/m field strengths. Affecting phenomena such as ice formation in super-cooled water (15), transport through biological cell membranes (16), (where potential differences are often of comparable magnitude), and electrohydrodynamic behavior, which is typically modeled assuming an unchanged local molecular structure (7).

The key observations in water bridges that motivated this study were: Density gradients (7% edge to core) observed using optical techniques (6), anisotropy observed in neutron scattering (9), optical birefringence from polarized light scattering (11, 12) and changes in the OH stretch vibration from Raman and infrared measurements (10, 13).

Neutron scattering experiments on a floating bridge of D_2O (8) have suggested an increase in scattered intensity at $Q \leq 2 \text{ \AA}^{-1}$ which may be associated with the existence of nano-scale-bubbles (or some other form of nano-scale density fluctuations). Yet a subsequent study by the same group suggests the intensity increase may have been an artifact due to H_2O contamination in the D_2O sample (9). The second neutron study found some anisotropy in the angular distribution of the scattered neutron intensity, although the effect was comparable to the size of the error bars (9). This anisotropy observed in the neutron, and polarized light scattering suggests a preferred orientation of the hydrogen bonded water molecules along the electric field, at a relatively low approximately 10^6 V/m field strength.

Experimentally it is known that water molecules exhibit strong voltage-dependent ordering in fields approximately 10^9 V/m, such as those found within a few molecular layers from the surface of an electrode (3). Similarly density functional theory calculations have shown that electric fields stretch the intermolecular hydrogen bonds in water clusters (17). Above a certain field-strength threshold, these bonds are broken and the water clusters form linear, branched or net-like structures. However, molecular dynamics simulations (18) on small cold water clusters in relatively weak electric fields approximately 10^5 V/m do not show any substantial structural changes. Instead the simulations show an increased molecular vibrational amplitude and molecular reorientation. Other molecular dynamics simulations have suggested that it is the polarization of hydrogen bonds that induces the formation of the water bridge above a threshold field of 1.2×10^9 V/m (19); which is much higher than the approximately 10^6 V/m required to form the bridge experimentally. Alternatively, it has been proposed that ordinary surface tension holds the bridge together rather than the electric field directly (20).

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charge, pair potential simulation is not intended to exactly reproduce the water structure within the bridge, instead the 10^9 V/m field strength was chosen to provide a benchmark aligned structure. Whereas the 10^6 V/m field strength simulation contained very little molecular alignment, and is expected to be more representative of the E-field in the floating water bridge. In order to calculate the simulated structure factors of the anisotropic liquid from these MD simulations we have to go beyond the spherical Bessel function approximation of Debye (23) [2]. Instead the structure factors of the MD simulations were calculated retaining the directions of the scattering vector \mathbf{Q} and pair separations $\mathbf{r}_{\alpha\beta}$ i.e.,

$$S_{ab}(\mathbf{Q}) - 1 = \frac{N}{N_a N_b} \left\langle \sum_{\alpha} \sum_{\beta \neq \alpha}^{N_a, N_b} \exp(i\mathbf{Q} \cdot \mathbf{r}_{\alpha\beta}) \right\rangle \quad [1]$$

$$\neq \frac{N}{N_a N_b} \left\langle \sum_{\alpha} \sum_{\beta \neq \alpha}^{N_a, N_b} \sin(Qr_{\alpha\beta}) / (Qr_{\alpha\beta}) \right\rangle. \quad [2]$$

Where $S_{ab}(\mathbf{Q})$, is the pairwise partial structure factor for chemical species a and b . N is the total number of atoms in the simulation box. N_a is the number of atoms of chemical species a . The summations are over all distinct pair combinations α, β in the simulation box, and the brackets $\langle \rangle$ denote that the thermal average is taken. The dot product is calculated using the fact that the magnitude of $|\mathbf{Q}| = Q = 4\pi \sin(\theta)/\lambda$, and is given from geometry by

$$\mathbf{Q} \cdot \mathbf{r} = -Q \sin(\theta) r_x + Q \cos(\theta) \sin(\phi) r_y + Q \cos(\theta) \cos(\phi) r_z. \quad [3]$$

Where ϕ is the angle of the \mathbf{Q} -vector from the vertical z -axis, and 2θ is the scattering angle from the x -direction of the incident beam (see Fig. 4A, *Inset*). This dot product method makes no assumptions about symmetries in the sample (see *SI Text* for derivation). In principle the directional structure factor of any arrangement of atoms can be reconstructed this way, without the need for small angle, isotropic, nor Bragg approximations. For these reasons it is preferred to other methods such as expanding the Bessel function approximation to higher orders (for example see refs. 24 and 25), which usually retain some symmetry assumptions. This calculation is also useful for this work as it directly provides the structure factors in the same \mathbf{Q} -space form as diffraction measurements.

The results of the directional structure factor analysis are plotted in Fig. 4B, which shows the oxygen-oxygen structure factors $S_{OO}(Q, \phi)$, for ϕ parallel and perpendicular to the applied electric field in the MD models. Because it contributes over 90% of the signal in the X-ray measurements, $S_{OO}(Q, \phi)$ was calculated at both 10^6 and 10^9 V/m field strengths. The large ϕ dependence of the directional $S_{OO}(Q, \phi)$ patterns in the 10^9 V/m MD model confirms the sensitivity of the $S_{OO}(Q, \phi)$ and hence $S^X(Q, \phi)$ to molecular alignment. The large ϕ dependence of the 10^9 V/m model is in contrast to the measured $S^X(Q, \phi)$, which was found to remain constant to within 2%, across all ϕ angles in the water bridge (Fig. 4A). The measured horizontal minus vertical differences in the water bridge were also essentially featureless in real space [Fig. 3, curve (D)]. For completeness the $S_{OH}(Q, \phi)$ and $S_{HH}(Q, \phi)$ of the 10^6 V/m MD model, are plotted in Fig. 4C. These oxygen-hydrogen (OH) and hydrogen-hydrogen (HH) partial structure factors contribute very little to the X-ray signal, but dominate neutron scattering patterns, and are expected to be more sensitive to molecular alignment than the OO distribution. Fig. 4C however, shows that like OO, the OH and HH structure factors at 10^6 V/m are isotropic, and equal to those of ambient water.

The similarity of the bridge water structure to ambient liquid water, and the lack of anisotropy, means that our results do not support the formation of any significant fraction of linear, chain-like structures within the bulk of the water bridge. This lack of anisotropy is also supported by previous theoretical studies where higher field strengths were required for alignment (26–29). The question therefore remains; how does the bridge form: If it is not a bulk structure effect, the answer probably lies in surface effects.

The effect of electric fields on the surface tension of water has been notoriously difficult to study and the results have been inconclusive with no general agreement (30–32). However, Bateni et al. have recently pioneered a new methodology to measure the surface tension of sessile droplets in electric fields (33, 34). They find that electric field strengths approximately 10^6 V/m increase the surface tension approximately 6%. This, and our bulk structure findings, support the conclusions of ref. 20 that relatively normal surface tensions are sufficient to provide the mechanical tension required. For example a 1 mm radius cylinder of water weighs approximately 3×10^{-4} N per centimeter of length, whereas the surface tension of ambient water is approximately 7×10^{-4} N/cm. Bateni et al. have also observed that the shape of water droplets changes significantly when a 5 kV electric potential is applied, acting against gravity (33, 34). This is in line with the electric field acting only on the surface to stabilize the shape of the water bridge, rather than affecting the bulk.

In conclusion we find the bulk structure of water within the floating water bridge to be isotropic, and the same as ordinary water at the same temperature. TIP4P/2005 MD calculations, at approximately the same field strength support this conclusion. The directional structure factor formalism given here is general, and does not require any symmetry assumptions of the sample. The lack of assumptions means that in principle any measured structure factor in a given ϕ -direction of any class of material can be directly compared to atomistic models. This method provides significantly more structural information, and a more stringent comparison to models, than traditional spherically averaged total scattering measurements. Some examples where this directional structure factor analysis may provide useful insight in future are amorphous and/or poorly crystalline fibers, liquid crystals, and disordered crystals.

Materials and Methods

The floating water bridge apparatus consisted of two 250 mL beakers, filled to within 5 mm of the top with 18 M Ω cm deionized water. One beaker was mounted on a translational stage, and the other was fixed. The beakers were placed so that the pouring lips were aligned, and platinum wire electrodes were placed in each beaker. A dc voltage, typically between 11 and 18 kV was applied to one electrode using a Trek P0621P, which was current limited to 0.5 mA. After a brief initial arcing, the water flowed up the beaker walls to connect and form a bridge. The movable beaker was slowly translated away from the other to extend the bridge length to between 5 mm and 25 mm. The surface temperature of the bridge was measured using two infrared thermal imaging cameras (Inframetrics model 760 and FLIR SC8000 series). The model 760 operated in the 8–12 micron range where the emissivity of water is known to be 0.96. The FLIR operated in the 3–5 micron range, and agreed with the model 760 measurement to within 2 °C implying an effective emissivity ≥ 0.9 for the 3–5 micron range used by the FLIR. The bridges were formed repeatedly over several days and typically remained stable for 30 min or more.

An incident X-ray beam with an asymmetric 0.2 mm (vertical) \times 0.5 mm (horizontal) rectangular cross-section was used. The Perkin Elmer XRD1621 flat plate area detector was off-centered 20 mm to avoid residual image effects from previous measurements, and placed 425–435 mm behind the sample. This setup provided a usable Q -range of 0.4–24 \AA^{-1} , from the beam-stop to the nearest detector edge. The 760 infrared camera was aligned to be coincident with the X-ray beam, whereas the FLIR infrared camera gave a simultaneous temperature measurement of the entire water bridge during the experiment (see Fig. 1). The water bridge was precisely aligned to the X-ray beam by measuring the X-ray transmission with a photodiode detector. This transmission measurement also provided the dimensions of the water bridges formed, which varied between 7–11 mm in length, and

0.8–1.3 mm in diameter. The sample-detector distance was determined using a CeO₂ filled, thin-walled polyimide capillary, which was placed across the beakers where the water bridge formed. Placement of the calibrant relative to the water bridge was confirmed to within 0.2 mm using a surveyors leveling scope. The X-ray scattering data were analyzed and the X-ray structure factors extracted using standard methods applied to large area detectors as described in refs. 21 and 35. The ambient liquid water data shown in Fig. 2 was measured separately from a vertically downward flowing stream of water approximately 3 mm wide, at the same X-ray beamline (details to be published elsewhere).

In this work, the $S^X(Q)$ patterns have had the intramolecular OH and HH contributions subtracted through use of the molecular form factor calculated in ref. 36. The $S^X(Q)$ patterns were weighted using the commonly used $w^X = |\sum_a c_a f_a|^2$, where c_a and f_a are the concentration, and form factors of element species a . This weighting function has the advantage that the total weighting in $S^X(Q) \approx 1$ for all Q -values. The form factors used to calculate the w^X weighting function were taken from ref. 37 and modified to account for charge redistribution from H toward O, using the formula suggested by refs. 38 and 39. The X-ray distribution function $D^X(r)$, is then obtained from the measured $S^X(Q)$ by sine Fourier transformation as follows.

$$D^X(r) = 2/\pi \int_{Q_1}^{Q_2} Q[S^X(Q) - 1] \sin(Qr) dQ. \quad [4]$$

Where Q_1 and Q_2 are the minimum and maximum measured Q -values (see refs. 35 and 40 for further detail and definitions). The higher number of electrons on oxygen vs. hydrogen, coupled with the redistribution of charge toward the oxygen in the O–H bond, results in an oxygen-oxygen weighting that varies from approximately 80% at $Q = 0$, to $\geq 95\%$ at $Q \geq 12 \text{ \AA}^{-1}$, in the X-ray measurements. This strong OO weighting is why the X-ray measurement essentially describes the distribution of molecule centers, with only a minor intermolecular OH contribution and negligible intermolecular HH contribution.

The MD structure in Fig. 4 was generated from a TIP4P/2005 (41) simulation on 1,000 water molecules, implemented within the DL_POLY classic MD package (42). The TIP4P/2005 potential was chosen because it reproduces

ambient liquid water structure more accurately than other empirical potential models (43). First principles, or DFT models were not considered, as the size of this simulation was required to be $\geq 1,000$ molecules to reproduce the experimentally observed Q and r ranges. The E-fields used in this fixed charge model were 10^6 and 10^9 V/m. The 10^9 V/m field strength simulation was not intended to reproduce the bridge structure, but was chosen to demonstrate the sensitivity of the directional structure factor technique to aligned water structures. To compare to the measured $S^X(Q, \phi)$, where ϕ was averaged over slices 10 degrees wide, the simulated $S_{OO}(Q, \phi)$, were also averaged from several ϕ points over the same range. Also, to reduce noise in both the simulation and measurements, 180 degree opposing ϕ -directions were averaged together. Because the MD model only calculates a full sphere of atom separations up to half the box side length (r_m), larger separations were neglected. This results in an $S(Q)$ which transforms to give a pair distribution function which is truncated to zero for $r \geq r_m$. To correct for the truncation we added the function $C(Q)$ to the $S(Q)$ calculated using [2] where

$$C(Q) = \frac{4\pi\rho(Q \cos(Qr_m) - \sin(Qr_m))}{Q^3}. \quad [5]$$

This $C(Q)$ is taken from ref. 45, and was chosen because its real space Fourier transform is a step function which =0 at and below r_m and =1 above r_m . Use of this $C(Q)$ function essentially substitutes the missing higher- r structural information, with the macroscopic density of the material; i.e., the assumption $g(r) = 1$ (or $D(r) = 0$), for $r \geq r_m$ is made. For the 1,000 molecule simulations performed in this work the $r_m \approx 15.5 \text{ \AA}$, where the distribution functions are already very close to the assumed macroscopic limit.

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