Experimental evidence of the ferroelectric phase transition near the \(\lambda\)-point in liquid water.

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We studied dielectric properties of nano-sized liquid water samples confined in polymerized silicates MCM-41 characterized by the porous sizes \(\sim 3-10\,\text{nm}\). We report the direct measurements of the dielectric constant by the dielectric spectroscopy method at frequencies \(25\,\text{Hz} - 1\,\text{MHz}\) and demonstrate clear signatures of the second-order phase transition of ferroelectric nature at temperatures next to the \(\lambda\)-point in the bulk supercooled water. The presented results support the previously developed polar liquid phenomenology and hence establish its applicability to model actual phenomena in liquid water.

Large dipole moments of individual molecules and the high density of water are reasons behind the very rich phase diagram and quite a few “anomalous” properties \([1]\). Understanding the dielectric response of the liquid plays a crucial role in modeling molecular interactions in computational physical chemistry, biophysics, and drug design applications \([2, 3]\). The static dielectric constant \(\varepsilon\) of water at room temperatures is very large, increases as the temperature decreases, and even diverges in supercooled water being extrapolated to the unreachable temperature \(T_C \approx 228^\circ\text{K}\) of the so called \(\lambda\)-transition \([4]\). Most other thermodynamic quantities, such as isothermal compressibility, density, diffusion coefficient, and viscosity, are also singular \([5, 6]\). Following the earlier idea of \([7]\), the authors of \([8, 9]\) indicated that the phase transition could have ferroelectric features. The ferroelectric hypothesis was also supported by a number of molecular dynamics (MD) simulations \([10, 11]\). For example, a ferroelectric liquid phase was observed in a model of the so-called “soft spheres” with static dipole moments \([12, 13]\). The conclusion seems to be model independently confirmed in the MD of hard spheres with point dipoles \([14, 15]\), soft spheres with extended dipoles \([16]\), and in a model of fluids made of two-state particles with a nonzero dipole in the excited state \([17]\).

Unfortunately, the relation of the ferroelectric phase transition to the \(\lambda\)-point in actual water or even the very existence of the paraelectric phase may be difficult to confirm in MD simulations with finite number of atoms. There are quite a few reasons to it. First of all due to the long range nature of the dipole-dipole interactions between the molecules, the simulated liquid tend to form tightly correlated domains and the calculated properties depend strongly on the boundary conditions in any reasonably sized system \([18]\). In the same time because of the low temperatures and the proximity of various phase transitions the relaxation processes take a very long time, which transforms into a necessity to simulate large and strongly interacting molecular systems in realistic forcefields for a very long time.

The same problems naturally hinder theoretical understanding of the physics behind the phase transition. There could be no purely electrostatic MD model of the phase transition, since classical systems with electrostatic interactions only are inherently unstable. Chemical forces, such as hydrogen bonds, are known to play a very important role in water molecule ordering at all temperatures in general, but particularly when close to the phase transition \([19, 20]\). The “minimal” continuous model capable of predicting finer effects depending both on the hydrogen bonding properties and the electrostatic interactions of the water molecules was proposed in \([21, 22]\). One of its predictions is the ferroelectric phase transition in liquid water within the temperature interval \(T_C = -37 \div -47^\circ\text{C}\), which is remarkably close to the \(\lambda\)-point. In \([10]\) the singularity of dielectric constant \(\varepsilon\) as extrapolated to the unreachable temperature \(T_C = -45^\circ\text{C}\) was indeed reported. On the other hand due to its weak character and unattainability of \(T_C\) the authors of \([10]\) did not attribute it to the a ferroelectric phase transition.

Fortunately the freezing temperature can be essentially lowered in water confined in nanopores (see \([23, 24, 25]\) and references therein). The porous systems can be studied by vapor pressure measurements \([26]\), dilatometry \([27, 28]\), calorimetry \([29, 30]\), nuclear magnetic resonance \([31, 32]\), neutron diffraction \([33, 34]\), small-angle neutron scattering \([35, 36]\), and X-ray diffraction \([37]\). The measured transition temperature depression can be approximated as \(\Delta T \approx -K/(R - t)\), where \(R\) is the characteristic radius of the pore, \(K = 52\,\text{K}\cdot\text{nm}\), and \(t = 0.4\,\text{nm}\) is the (empirical) hydration layer thickness \([38]\). Already for the pore radii below \(R \sim 2\,\text{nm}\) the decrease in freezing temperature can be as large as \(-50\,\text{K}\) and hence the predicted ordering phase transition at \(T = T_C\) can be observed and studied experimentally. Moreover, in hindsight we believe that the first signatures of such a transition were already observed in \([39]\). In this work we present the results of the direct measurements of the low-frequency liquid water dielectric constant, \(\varepsilon\), in nanopores by dielectric spectroscopy method. The observed singularity of \(\varepsilon\) near the \(\lambda\)-point temperature in the supercooled bulk water is a clear signatures of the second-order transition of ferroelectric nature, both
in quantitative and qualitative agreement with the polar liquid phenomenology.

The polar liquid phenomenology \cite{31} extends the continuous models \cite{21,54-61} and was originally developed to describe electrostatic energies of biomolecules in aqueous solutions for drug discovery applications \cite{62}. The model naturally describes the ordering phase transition in water \cite{39,62}. Within the suggested model the polar liquid is characterized by the vector-field \( \mathbf{s}(\mathbf{r}) = (d(\mathbf{r})) / d_0 \), where \( \mathbf{d}(\mathbf{r}) \) is the vector of the static dipole moment of molecule residing at point \( \mathbf{r} \), \( d_0 \) is its absolute value, \( 0 < s(\mathbf{r}) < 1 \). Total dipole moment of molecule equals \( \mathbf{d}_s(\mathbf{r}) = \mathbf{d}(\mathbf{r}) + \mathbf{d}_e(\mathbf{r}) \), where \( \mathbf{d}_e(\mathbf{r}) \) is the dipole moment induced in the electronic shell. The Helmholtz free energy of polar liquid is described by the functional of independent variables \( s(\mathbf{r}) \) and \( \mathbf{d}_e(\mathbf{r}) \):

\[
F(\mathbf{s}(\mathbf{r}), \mathbf{d}_e(\mathbf{r})) = P_0^2 \int dV \left( \frac{C}{2} \sum_{\alpha,\beta} \frac{\partial s_{\alpha}}{\partial x_{\beta}} \frac{\partial s_{\alpha}}{\partial x_{\beta}} + V(s^2) \right) + \int dV \frac{2\pi d_0^2}{(\epsilon_\infty - 1)} + \int dV \frac{1}{8\pi} E_P^2 - \int dVP(\mathbf{r}) E_e(\mathbf{r})
\]

(1)

Here \( C \) is the phenomenological parameter responsible for the \( H \)-bond network rigidity, \( P_0 = n_0 d_0 \), \( n_0 \) is the particle density of the liquid, \( \epsilon_\infty \) is the part of the dielectric constant of the liquid which is unrelated to the molecular rotations and accounts properly for the polarization of the internal (e.g. electronic) degrees of freedom. It is the dielectric constant at frequencies larger than that correspond to reorientation of molecules. Next, \( \mathbf{E}_P = -\nabla \varphi_P \) is the polarization electric field produced by the polarization charges with a density \( \rho_P = -\nabla \mathbf{E}_P \) (sometimes it is called as the depolarizing field), \( \mathbf{E}_e(\mathbf{r}) = -\nabla \varphi_e \) is the external electric field induced by external charges with the density \( \rho_e(\mathbf{r}) \), \( \mathbf{P}(\mathbf{r}) = P_0 s(\mathbf{r}) + n_0 \mathbf{d}_e(\mathbf{r}) \) is the polarization vector of liquid at point \( \mathbf{r} \), \( \mathbf{E}(\mathbf{r}) = \mathbf{E}_P(\mathbf{r}) + \mathbf{E}_e(\mathbf{r}) \) is the total electric field at point \( \mathbf{r} \), \( \varphi = \varphi_P + \varphi_e \). Electric potentials \( \varphi_P \) and \( \varphi_e \) should be found from correspondent Poisson equations \( \Delta \varphi_P = -4\pi \rho_P \), \( \Delta \varphi_e = -4\pi \rho_e \).

The phenomenological dimensionless function \( V(s^2) \) serves as the polar liquid equation of state and can not be established in general form. Its specific form can be found by comparing the model results obtained with the help of Eq.\,(1) with the results of MD simulations of a specific liquid. On the contrary, in the small \( s^2 \ll 1 \) limit the function takes a nearly universal form: \( V(s^2) \approx 4\pi s^2 / (3\epsilon_\infty) \) has a universal (i.e. the same for any polar liquid) form, \( B = 3\pi / (5\epsilon_\infty) \) is a liquid-specific constant, \( B \sim 1 \), and \( \tau = (T - T_c) / T_c \), where, at last, \( T_c = 4\pi n_0 d_0^2 / 9\epsilon_\infty \)

(2)
is the critical temperature within the model. The physical picture behind the change of the coefficient \( A \) sign can be recovered from the following argument. For uniformly polarized liquid, \( s(\mathbf{r}) = \text{const} \), the free energy takes Landau-like form \cite{63}:

\[
F = V \frac{P_0^2}{2} \left( \frac{2\pi T}{3\epsilon_\infty} s^2 + B s^4 \right).
\]

At temperatures \( T > T_C \) the equilibrium state correspond to the disordered paraelectric phase with \( (s) = 0 \), whereas at lower temperatures \( T < T_C \) the polar liquid undergoes the second order phase transition and transforms to the long-range ordered ferroelectric state.

Second order ferroelectric phase transition should manifest itself as a singularity in the liquid dielectric constant \( \epsilon \). To analyze the dielectric response we apply a uniform electric field \( \mathbf{E} \) and calculated the polarization of the liquid by the minimization of free energy \cite{1}:

\[
2V'(s^2) s = \frac{1}{P_0^2} \mathbf{E}, \quad \mathbf{d}_e = \frac{\epsilon_\infty - 1}{4\pi n_0} \mathbf{E}
\]

(3)

Consequently, in the weak electric field limit \( E \ll P_0 \) at \( |\tau| \ll 1 \) the static dielectric constant of the liquid is given by:

\[
\epsilon = \epsilon_\infty \left( 1 + \frac{3}{\tau} \right), \quad T > T_C; \quad \epsilon = \epsilon_\infty \left( 1 + \frac{3}{2|\tau|} \right), \quad T < T_C.
\]

(4)

Therefore the measurements of the temperature dependence in \( \epsilon(T) \) should exhibit a \( \lambda \)-point feature and diverge at \( T = T_C \). The exact value of the critical temperature for water can be obtained using either of a few published measurements of the asymptotic values: \( \epsilon_\infty \approx 4.9 \) from \cite{64}, \( \epsilon_\infty = 5.1 \) from \cite{65}, or \( \epsilon_\infty = 5.5 \) from \cite{66}. Respectively, Eq.\,(2) gives \( T_c = 236K \) (\(-37^0C\)), \( T_c = 226K \) (\(-47^0C\)), and \( T_c = 210K \) (\(-63^0C\)). All the numbers are remarkably close to \( T_c \approx 228K \) or \( T_c \approx 231K \) measured in supercooled bulk water \cite{10}.

To resolve the issue we investigated the dielectric response of the water samples confined in polymerized silicate MCM-41 characterized by a typical pore diameters
of $D \approx 3 \div 10\,\text{nm}$ \cite{72,68}. We used the dielectric spectroscopy method at frequencies range 25Hz-1MHz. The results of the measurements are summarized on Fig.1 and show a very distinguished $\lambda$-feature at $T_{C}^{exp} \approx -35^\circ\text{C}$ in full accordance the second-order phase transition picture presented above. At first glance at large temperatures the data seem to suggest a rise of $\epsilon$ with temperature in contradiction to both earlier experiments \cite{10} and the theoretical prediction \cite{4}. In fact the measurement errors in the dielectric spectroscopy experiment are quite large and the contradiction disappears entirely when the close vicinity to the transition point is considered. Next to the observed transition temperature the singularity of $\epsilon$ is much stronger than the previously reported dependence $\epsilon \propto |\tau|^{-\alpha}$ characterized by the critical index $\alpha \approx 0.13$ \cite{10}. The mean field theoretical prediction $\alpha = 1$ results in a much better agreement with the measured values. Close to the phase transition one can consider using a more more refined approach. Indeed, when $|\tau| \ll 1$, the fluctuations in the model \cite{1} are “force”-less, $\nabla \cdot \mathbf{s} = 0$, $\rho_{P} = 0$, $\mathbf{E}_{P} = 0$ \cite{31}, the dipole-dipole interactions vanish and the scale invariant calculation from \cite{69} gives $\alpha \approx 1 + (4 - d)/6$, where $d$ is the number spatial dimensions. Actually $d = 3$ and $\alpha = 7/6 \approx 1.2$, which gives is stronger singularity than in the mean field theory. Though it is hard to tell from a few points we have, the experimental divergence of $\epsilon$ on Fig.1 appears even stronger than each of the theoretical predictions. This should not be surprising since our model is indeed over-simplified. The calculations can be further improved by including at least the two important forms of the liquid water states (such as the hexagonal and the cubic water structures as explained in e.g. \cite{70,71}). If we associate the ferroelectric phase transition with a single (say, cubic \cite{16}) component only, then the critical behavior of the dielectric constant may be changed quite dramatically by the sharp temperature dependence of the cubic water fraction \cite{72}.

The hydration thickness $R_{D} \ll t \lesssim L_{T}$, where $R_{D} \approx 0.2\,\text{nm}$, and $L_{T} \approx 0.7\,\text{nm}$ are characteristic phenomenological scales of the liquid characterizing roughly the water molecules cluster and the maximum correlated domain sizes respectively \cite{39,32}. Thus the pores in MCM-41 are very large compared to the hydration layer thickness, $D \gg t, L_{T}$, and therefore the water in nanopores still has all the properties of the bulk water. The equilibrium freezing temperature of water in MCM-41 systems with $D = 3.5\,\text{nm} \approx -35^\circ\text{C} < T_{C}^{exp}$ \cite{53} and therefore the water samples in our experiments are still liquid at temperatures $T \sim T_{C}^{exp}$ near the $\lambda$-point. The liquid and the solid water states were definitely distinguished using the hysteresis effect \cite{5,48,73}: the solid curve on Fig.1 corresponds to the supercooled liquid state and the dashed line describes the dielectric properties of the overheated ice state.

In this way water freezing temperature suppression and the hysteresis phenomena typical for water in nanopores let us actually investigate the properties of the supercooled bulk liquid water in the temperature range $-70 \div +23^\circ\text{C}$. The dielectric spectroscopy measurements reveal the strong singularity in dielectric constant at temperatures corresponding to the position of $\lambda$-point of the bulk water. Therefore the experimental data point support the earlier theoretical predictions \cite{30,32} of existence of the second order phase transition of ferroelectric nature. Eq.\,(2) reconcile earlier theoretical predictions of \cite{24} with the experimentally observed values for the phase transition temperature by introducing electronic polarizations $\epsilon_{\infty}$. The very fact that the dielectric constant singularity was actually observed suggests that experiments with water in nanoporous materials can be used for in-depth studies of complicated phase diagram of water.

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