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Experimental evidence of the ferroelectric nature of the λ-point transition in liquid water

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We studied the dielectric properties of nano-sized liquid water samples confined in polymerized silicates MCM-41 characterized by pore sizes 3–10 nm. Freezing temperature suppression in nanopores helps keep the water samples in liquid form at temperatures well below 0 °C and thus effectively study the properties of supercooled liquid water. We report the first direct measurements of the dielectric constant by the dielectric spectroscopy method and demonstrate very clear signatures of the second-order phase transition of ferroelectric nature at temperatures next to the λ-point in the supercooled bulk water in full agreement with the recently developed model of the polar liquid.

Strong hydrogen bonds between and large dipole moments of individual molecules are reasons behind the very rich phase diagram and quite a few "anomalous" properties [1–7]. Understanding the dielectric response of the liquid plays a crucial role in modeling molecular interactions in computational physical chemistry, biophysics, and drug design applications [8]. The static dielectric constant ϵ of water at room temperatures is very large, increases as temperature decreases, and even diverges in supercooled water if the measured values are extrapolated to the temperature $T_C \approx 228\,\mathrm{K}$ of the λ-type transition [9, 10]. Unfortunately, this temperature is unreachable in the bulk water due to fast bulk nucleation. Most other thermodynamic quantities, such as isothermal compressibility, density, diffusion coefficient, and viscosity, are also singular [9–11]. Following the earlier idea of [12], the authors of [13, 14] indicated that the phase transition could have ferroelectric features. The ferroelectric hypothesis was also supported by a number of molecular dynamics (MD) simulations in various model polar liquids (see e.g. [15–17]). For example, a ferroelectric liquid phase was observed in a model of the so called "soft spheres" with static finite size dipole moments inside the spheres [15, 17–20]. The conclusion seems to be a model-independent and confirmed in the MD of hard spheres with point dipoles [18, 21].The ferroelectric state of Stockmayer fluid was studied in [22].

Unfortunately, the relation of the ferroelectric phase transition (FPT) to the λ-point in actual water, or even the very existence of the paraelectric phase, may be difficult to confirm in MD simulations with a finite number of particles. There are quite a few reasons for this. First of all, due to the long range nature of the dipole-dipole interactions between the molecules, the simulated liquid tends to form tightly correlated domains and the calculated properties depend strongly on the boundary conditions in any reasonably sized system [17]. At the same time, because of the low temperatures and the proximity of various phase transitions, the relaxation processes take a very long time [23]. This leads to a necessity for simulating large and strongly interacting molecular systems in realistic force-fields for very extended periods of time.

The same problems naturally hinder the theoretical understanding of the physics behind the phase transition. There could be no purely electrostatic 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 transitions [24, 25]. The "minimal" continuous model capable of predicting finer effects depending on both the hydrogen bonding properties and the long-range dipole-dipole interactions of the water molecules was proposed in [26–28]. One of its predictions is the FPT in liquid water within the temperature interval $T_C = -(37 - 47)\,^\circ\mathrm{C}$, which is remarkably close to the experimentally observed λ-point. In [10], a nearly divergent temperature dependence of dielectric constant ε near λ-point was indeed reported. On the other hand, due to weak character of the divergence and factual unattainability of T_C, the λ-features in the experiments were not attributed it to the FPT.

Fortunately, the freezing temperature can be essentially lowered in water confined in nanopores (see

[5, 6, 29, 30] and references therein). Already for a pore of a radius $R \leq 2$ nm, the decrease in freezing temperature can be as large as -50 K [29] and hence, the predicted ordering phase transition at $T = T_C$ can be observed and studied experimentally. Ferroelectric ice-XI state exists in the water bulk according to [4]. Similarly the ferroelectric phase is predicted in MD simulations of the liquid water and ice in nanotubes [31, 32] and in water shells around proteins [33]. The water in the porous systems can be studied by numerous methods (see e.g. [6] for a review). In this work, we present the results of the direct measurements of the low-frequency dielectric constant ϵ of water in nanopores obtained using the dielectric spectroscopy method (DSM) [34]. The data were obtained in MCM-41 samples with the pore diameters $D = 3.5$ nm, which is much larger than the hydration layer thickness (~ 0.4 nm [29]). This means that the phase transition and the ordering properties of the liquid in our experimental system are very close to that of the bulk liquid at the same temperature [35–38].

The polar liquid phenomenology [27] extends the continuous models [39–43] and was originally developed to describe electrostatic energies of biomolecules in aqueous solutions for drug discovery applications [44]. The model naturally describes the ordering phase transition in water [26, 28]. Within the suggested model, the polar liquid is characterized by the vector-field $\mathbf{s}(\mathbf{r}) = \langle \mathbf{d}(\mathbf{r}) \rangle / d_0$, where $\mathbf{d}(\mathbf{r})$ is the vector of the static dipole moment of a molecule residing at point $\mathbf{r}$, d_0 is its absolute value, $0 < s(\mathbf{r}) < 1$. The total dipole moment of the molecule equals $\mathbf{d}_t(\mathbf{r}) = \mathbf{d}(\mathbf{r}) + \mathbf{d}_e(\mathbf{r})$, 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 fields $\mathbf{s}(\mathbf{r})$ and $\mathbf{d}_e(\mathbf{r})$:

$$F(\mathbf{s}(\mathbf{r}), \mathbf{d}_e(\mathbf{r})) = P_0^2 \int dV \left(\frac{C}{2} \sum_{\alpha,\beta} \frac{\partial s_\alpha}{\partial x_\beta} \frac{\partial s_\alpha}{\partial x_\beta} + V(\mathbf{s}^2) \right) + \\ + \int dV n_0^2 \frac{2\pi \mathbf{d}_e^2}{(\epsilon_\infty - 1)} + \int dV \frac{1}{8\pi} \mathbf{E}_P^2 - \int dV \mathbf{P}(\mathbf{r}) \mathbf{E_e}(\mathbf{r}). \tag{1}$$

Here, C is the phenomenological parameter characterizing the H-bond network rigidity, $P_0 = n_0 d_0$, n_0 is the particle density of the liquid. Electrons are considered in frames of the "jelly" model as a continuous medium with dielectric constant ϵ_∞. Next, $\mathbf{E}_P = -\nabla \varphi_P$ is the polarization electric field produced by polarization charges with a density $\rho_P = -\nabla \mathbf{P}$ (sometimes called the depolarizing field), $\mathbf{E}_e(\mathbf{r}) = -\nabla \varphi_e$ is the external electric field induced by external charges with the density $\rho_e(\mathbf{r})$, $\mathbf{P}(\mathbf{r}) = P_0 \mathbf{s}(\mathbf{r}) + n_0 \mathbf{d}_e(\mathbf{r})$ is the polarization vector of liquid at point $\mathbf{r}$, and $\mathbf{E}(\mathbf{r}) = \mathbf{E}_P(\mathbf{r}) + \mathbf{E}_e(\mathbf{r}) = -\nabla \varphi$ is the total electric field at point $\mathbf{r}$, $\varphi = \varphi_P + \varphi_e$. Electric potentials φ_P and φ_e should be found from the corresponding 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 a general form. Its specific form can be found by comparing the model results obtained from 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: $V(s^2) \approx As^2/2 + Bs^4$, $A = 4\pi\tau/(3\epsilon_\infty)$, and $\tau = (T - T_C)/T_C$. Coefficient A has a universal form, whereas $B \sim 1$ is a liquid-specific constant. At last,

$$T_C = \frac{4\pi n_0 d_0^2}{9\epsilon_\infty} \tag{2}$$

is the critical temperature within the model. The significance of T_C can be clarified from the following argument. For uniformly polarized liquid $\mathbf{s}(\mathbf{r}) = \text{const}$, the free energy (1) takes on a Landau-like form:

$$F = V \frac{P_0^2}{2} \left(\frac{2\pi\tau}{3\epsilon_\infty} s^2 + Bs^4 \right).$$

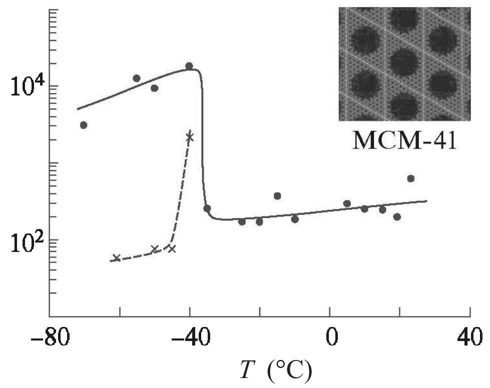
At temperatures $T > T_C$, the equilibrium state corresponds to the disordered paraelectric phase with $\langle \mathbf{s} \rangle = 0$, whereas at lower temperatures $T < T_C$, the polar liquid undergoes the second order phase transition and transforms to the long range ordered ferroelectric state.

The second order FPT should manifest itself as a singularity in the liquid dielectric constant ϵ (see e.g. [45]). The static dielectric constant of the liquid in a weak uniform electric field $\mathbf{E}$ can be calculated by the minimization of free energy (1) in the presence of the field:

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

Therefore, the measurements of the temperature dependence in $\epsilon(T)$ should exhibit a λ-point feature and diverge at $T = T_C$. The exact value of the critical temperature for water can be obtained by using any of the following published measurements of the asymptotic values: $\epsilon_\infty = 4.9, 5.1, 5.5$ from [46–48], respectively. Accordingly, for each of the reported values Eq. (2) gives $T_C = 236$ K (-37 °C), $T_C = 226$ K (-47 °C), and $T_C = 210$ K (-63 °C). All the numbers are remarkably close to $T_C \approx 228$ K [9–11], measured in supercooled bulk water. This view is in fact qualitatively supported by MD calculations of model liquids made of hard spheres [15–17], where the FPT was also observed though at very high temperatures, corresponding to $T_C \sim 10^3 K$. In our judgment this is the reason why the ferroelectric hypothesis of th $\lambda-$point has not been widely accepted. Our more accurate calculations do take the electronic polarization of the particles comprising the liquid into account properly and provide a much better agreement of the model Eq.(2) with the experiment.

To figure out if actual water undergoes a FPT similar to that described by the model (1), we investigated the



Temperature dependence of low-frequency real part of dielectric susceptibility of liquid water (solid curve) and ice (dashed) in MCM-41 pores (see the inset for a microscopic scheme of the pores structure) with diameters 3.5nm

dielectric response of the water samples confined in polymerized silicate MCM-41 [49] characterized by a typical pore diameter of $D \sim 3{-}10$ nm [50, 51]. We used the DSM at frequency range 25Hz–1MHz. The results of the measurements are summarized in Fig. and show a very distinguished λ-feature at $T_C^{\rm exp} \approx -35\,^\circ$C in full accordance with the second-order phase transition views presented above. At first glance, at high temperatures, the data seems to suggest a rise of ϵ with temperature, which contradicts both earlier experiments [10] and the theoretical prediction (3). In fact, the measurement errors in the dielectric spectroscopy experiment are quite large and the contradiction disappears entirely when a close proximity to the transition point is considered. Next to the observed transition temperature, the singularity of ϵ is much stronger; it is stronger than a much weaker dependence $\epsilon \propto |\tau|^{-\alpha}$ characterized by the critical index $\alpha \approx 0.13$ previously reported in experiments with supercooled water [10]. The mean field theoretical prediction (3) $\alpha = 1$ results in a much better agreement with the measured values. Near the phase transition, one can consider using a more refined approach, which gives a stronger singularity than that in the mean field theory. Indeed, when $|\tau| \ll 1$, the fluctuations in the model (1) are “force-less”, $\nabla \cdot \mathbf{s} = 0$, [27], the dipole-dipole interactions vanish and the scale invariant calculation from [52] gives $\alpha \approx 1 + (4-d)/6 \approx 1.2$, where $d = 3$ is the number of spatial dimensions. Though it is hard to tell from the few experimental points we have, the divergence of ϵ on Fig. appears even stronger than each of the theoretical predictions. This should not be surprising since our model is indeed oversimplified. The accuracy of the calculations can be further improved using the liquid-liquid phase transition models [53–55] by including more of the liquid water phases (such as the hexagonal and the cubic water structures). If we associate the FPT with a single (say, cubic [14]) 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 [56].

Equilibrium freezing temperature of water in MCM-41 with pore diameters $D = 3.5$ nm is $-49\,^\circ\mathrm{C} < T_C^{\rm exp}$ [5] and therefore, the water samples in our experiments are still liquid at temperatures $T \sim T_C^{\rm exp}$ near the λ-point. The liquid and solid water states were definitely distinguished using the hysteresis effect [5, 57, 58]: the solid curve in Fig. corresponds to the supercooled liquid state down to the freezing temperature (at least down to $-44\,^\circ$C: it is not surprising that hysteresis effect depends on the experimental procedure), and the dashed line describes the dielectric properties of the overheated ice state up to the melting temperature. The dashed curve singularity on Fig. clearly shows that the very essential fraction of the ice in the pore is formed in the ferroelectric state. We can not infer which particular ice state is produced in the experiments. In fact, due to the ferroelectric ordering the free energy of cubic water state at sufficiently low temperatures can be lower than that of hexagonal state. Therefore, the cubic water fraction should increase as the temperature decreases in full agreement with observations [56, 57].

Hence, the water freezing temperature suppression and the hysteresis phenomena typical for water in nanopores lets us investigate the properties of the bulk liquid water in the temperature range $(-51){-}(+23)\,^\circ$C. The dielectric spectroscopy measurements reveal strong singularity in the dielectric constant at temperatures close to the λ-point of the bulk water. This is a direct and unambiguous signature of FPT in full agreement with the suggested theoretical picture. Earlier neutron and X-ray scattering experiments do provide evidence of the rearrangements of the microscopic water configurations of the confined water [56]. Since the dielectric properties have not been measured the nature of the spatial molecular structure transformations and the FPT itself could not be revealed. Our experimental data strongly supports the ferroelectric hypothesis from [26, 28] and are in a good agreement with the theoretical estimates for T_C. The observation of FPT behind the λ-point establish the general validity of the previosly developed polar liquid phenomenology and its applicability for practical calculations of aqueous systems of nm-sizes.

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