

# Application of the two-liquid model for the interpretation of the observed electrophysical properties of supercooled water in nonopores

*P. O. Fedichev<sup>1)</sup>, L. I. Menshikov<sup>+</sup>*

*Quantum Pharmaceuticals Ltd, 125171 Moscow, Russia*

*<sup>+</sup>The National Research Center “Kurchatov Institute”, 123182 Moscow, Russia*

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We propose a model combining the first-order liquid-liquid and the second-order ferroelectric phase transitions phenomenology to explain various features of the  $\lambda$ -point of liquid water. We suggest that the long-range dipole-dipole interaction of water molecules leads to a ferroelectric phase transition, which occurs only in the low-density component of the liquid and is the origin of the singularity of the dielectric constant recently observed in experiments with supercooled liquid water in nano-porous materials. Finally, we establish the model parameters and prove the consistency of the combined model by comparing its predictions with experimental data and the results of recent MD simulations.

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**1. Introduction.** At normal pressures near the  $\lambda$ -point at temperatures close to  $T_\lambda \approx 228$  K many thermodynamic quantities of supercooled water, such as heat capacity, compressibility, thermal expansion, and dielectric constants, exhibit nearly singular behavior [1–3]. However, the observed features are often weak, which suggests a thermodynamic continuity of the various water states near the  $\lambda$ -point [4, 5]. The intrinsic thermodynamic instability of liquid water at temperatures well below the freezing point has been a major obstacle both in experimental studies and theoretical modeling (see e.g. [6–13] for a review). The currently accepted view is to ascribe the  $\lambda$ -point features to a first-order Liquid-Liquid Phase Transition (LLPT). The model predicts the existence of a second critical point of water at the temperature  $T_{CR} \sim 200$  K and pressure  $\sim 1$  kbar [14–16]. The sharp temperature dependencies observed near  $T_\lambda$  are attributed to crossing the Widom line [17], where the density and entropy fluctuations are large [18]. The view is supported by numerous molecular dynamics (MD) simulations based on realistic water models [14, 19–28] simplified analytical models [29–33], and experimental studies [6, 34–37].

Recent MD studies have demonstrated that heat capacity and thermal conductivity [38] peak around  $T_\lambda$ , and that the liquid shows a good deal of ordering in the vicinity of the  $\lambda$ -point. Moreover, there have been studies demonstrating a number of dynamic property anomalies, such as loss of the Einstein relation between

diffusion and mobility coefficients [39, 40] and non-Arrhenius behavior of the liquid [17, 40, 41]. Similarly, recent experiments with supercooled water in nanopores also show a profound jump (in  $\sim 200$  times) in the dielectric constant,  $\epsilon(T)$ , near the  $\lambda$ -point [42, 43, 44]. According to [45], for example, it is a feature of the Ferroelectric Phase Transition (FPT). Together, the findings paint a much richer picture than a mere LLPT and, in fact, bring back an old idea [3] relating the weak singularity of the dielectric constant to a FPT. Remarkably, the hypothesis was put forward immediately after the discovery of the  $\lambda$ -point, but the weakness of the observed singularities prompted the authors [3] to reject the explanation. It is interesting that the experimentation with bulk water did not allow authors [3] to overcome only few degrees in cooling and to observe the great singularity in  $\epsilon(T)$ . It becomes possible in nanoporous materials. A model polar liquid consisting of freely rotating molecules with point dipoles, pair-wise interactions, and parameters similar to those of water predicts the FPT at a very high and essentially unreachable temperature,  $\sim 1200$  K [46]. Once the electron shell polarization,  $\epsilon_\infty \approx 4$  to 5 [47–49], is included we obtain a more sophisticated model [50, 51] giving a smaller FPT temperature

$$T_F = \frac{4\pi n_0 d_0^2}{9\epsilon_\infty} = (210-236) \text{ K} \approx T_\lambda, \quad (1)$$

where  $n_0$  is the density and  $d_0$  are the static dipole moments of the molecule comprising the liquid.

<sup>1)</sup>e-mail: peter.fedichev@gmail.com

Despite bringing the FPT temperature remarkably close to  $T_\lambda$ , the simple FPT model fails to reproduce the observed  $\epsilon(T)$  dependence. At higher temperatures, the simple FPT model predicts a slower rate of decrease than both older [3] and recently obtained empirical results [42–44]. This should not be surprising, since water is more complex than a model polar liquid consisting of point dipoles. The tetrahedral geometry of water molecule leads to a polyamorphism phenomenon [52, 6, 9], permitting two or more phases of the same liquid to exist in a mixture at the same time. In this paper, we develop a unified theoretical description aiming to provide a synthetic model mixing the LLPT and FPT phenomenology into a single theoretical framework and provide arguments that FPT is possible in frames of LLPT approach.

**2. The model.** We combine the “standard” LLPT [14, 15, 6] model in the form of the two-state model of liquid water developed in [53, 54] with the polar liquid [50, 42, 51] phenomenology. Accordingly, we assume that the equilibrium state of supercooled water is a mixture of macroscopically-sized clusters of the two types: the low density liquid (LDL) and the high density liquid (HDL). This viewpoint is the well-known mixture model [6, 26] and is well supported by the experiments [35, 36, 55].

We further assume that the FPT occurs in the LDL only, while the HDL phase has no ferroelectric state. We have two reasons for these assumptions. First, LDL is “softer” locally than HDL, since the density of LDL is about 20% less than HDL [6, 56–60]. Therefore, it seems natural to think that the molecules of LDL are capable to rotate more or less freely, whereas in the HDL the rotations are more difficult. Thus, LDL is closer to the pair-wise and isotropically interacting liquid used to derive Eq. (1). The possibility of FPT in LDL can be further supported by the structural similarity between the local structure of LDL and the crystalline lattice of the stable (paraelectric) phase of ice, ice Ih [61, 62]. According to some early observations [63–66] at normal pressures at temperatures below  $T \sim 70$  K the ice Ih enters the ferroelectric state, ice XI. Since LDL is less dense than the ice 1h, the FPT in LDL occurring at a much higher temperature is not surprising. But it is worth to note here that the existence of FPT in ice is not yet proved finally. Its possibility is supported by MD simulations (see, for example, [67, 68]), but the result is sensitive to the water model taken [68]. Pro and contra arguments were presented in [69]. Recent detailed simulations [70, 71] are in favor of the FPT. Main obstacle for the reliable experimental conclusions is the very long relaxation of the ferroelectric

states [72], therefore it was assumed that bulky ferroelectric ice exists only on remote planets [73]. FPT in ice was observed recently in neutron experiments [74].

The assumption of freely rotated molecules in LDL can be difficult to assume, because traditionally is supposed that the water properties are governed by the H-bond network [75]. In fact, at intermolecular distances in water,  $\bar{r} \sim 0.3$  nm, it is impossible to single out H-bond and dipole-dipole interactions,  $u_{dd}$ , from the total interaction between molecules, which has mostly the electrostatic nature. Two values is useful to present here to clear the situation: the enthalpy of water dimer formation is  $\Delta H = (12–15)$  kJ/mol [76, 77], and  $u_{dd} = 2d_0^2/\bar{r}^3 = 15$  kJ/mol for molecules with parallel dipoles. These estimates show that the dipole-dipole interaction is enough strong to influence essentially on the molecular orientations. At least, some of four spatial directions selected for each molecule by the H-bond network can be energetically preferable in LDL due to the long-range dipole-dipole interactions that is enough to establish the ferroelectric order.

Due to the hydrogen bonding there exists an approximate order such that the water molecules at small distances form lattice-like structures [75, 16]. The Gibbs free energy of an LDL cluster at a given pressure  $P$  is the sum of the contributions from the polar (rotational),  $G_{\text{LDL}}^P$ , and the lattice degrees of freedom,  $G_{\text{LDL}}^L$ :  $G_{\text{LDL}} = G_{\text{LDL}}^P + G_{\text{LDL}}^L$ . At higher temperatures,  $T > T_F$ , the equilibrium state of LDL corresponds to the disordered paraelectric phase, whereas at lower temperatures,  $T < T_F$ , the LDL phase becomes the long-range-ordered ferroelectric state. The free energy per mole takes the usual Landau form near the phase transition [78]:

$$G_{\text{LDL}} \approx -D\tau^2\theta(-\tau) + G_{\text{LDL}}^L(T, P), \quad (2)$$

where  $D \sim V_0 n_0^2 d_0^2 \sim 150$  cal/mol,  $\tau = (T_F - T)/T_F \ll 1$ , and  $V_0 = N_A/n_0 \approx 22$  cm<sup>3</sup> is the molar volume of LDL. The FPT manifests itself as a singularity of the dielectric constant  $\epsilon$  [45], which means that the dielectric constant of LDL is:

$$\epsilon = \epsilon_\infty [1 + f(T)], \quad (3)$$

where  $f(T) = 3T_F/(T - T_F)$  for  $T > T_F$  and  $f(T) = 3T_F/2(T_F - T)$  for  $T < T_F$ .

Following [53, 54], we represent the Gibbs energy of water in the form

$$G(c) = cG_{\text{LDL}} + (1 - c)G_{\text{HDL}} + Uc(1 - c) + RT [c \log c + (1 - c) \log (1 - c)]. \quad (4)$$



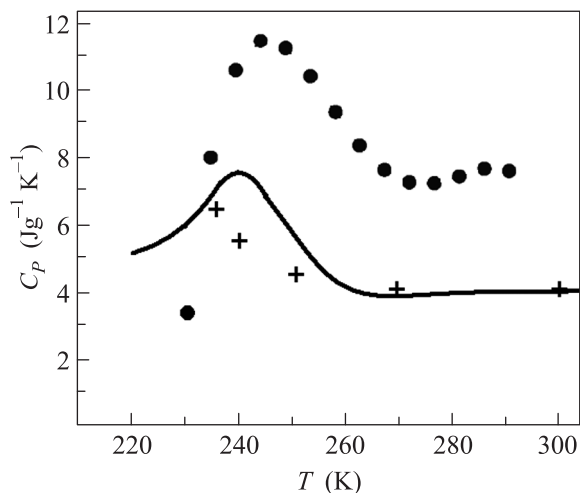


Fig. 2. The heat capacity of water (see Eqs. (7), (8), and (10); solid curve) vs. MD calculations [38] (points) and the empirical data [1] (crosses)

than HDL [38]. This also means that the FPT could have already been implicitly present in the MD.

Once the model parameters (10) are established, we can verify the consistency of the model by observing the temperature dependence of the LDL fraction  $c(T)$  given by Eq. (5) (see the solid line 1 in Fig. 3). There is

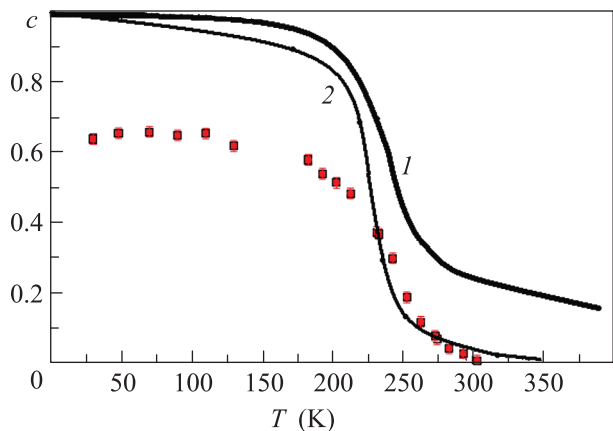


Fig. 3. Theoretical temperature dependence of the LDL fraction (solid lines, see the explanations in the text) versus empirical data [36] (dots)

a qualitative agreement between the predicted and the empirical data [36] (the dots) at sufficiently large temperatures above 200 K. We note that  $\Delta G(P, T = 0) < 0$  and, therefore, at sufficiently low temperatures all of the liquid should turn into LDL ( $c \rightarrow 1$  as  $T \rightarrow 0$ ). This implies that the equilibrium composition of water was not actually achieved in the experiments, especially at the lower temperatures. This may be due to the increase of the equilibration times; see, e.g., [80, 81]. Hence, we can

attempt to match the LDL fraction measurements at higher temperatures only, and we obtain a better agreement with the experiment using a slightly different parameter set (see solid line 2):

$$\Delta E^0 = -920 \text{ cal} \cdot \text{mol}^{-1}, \quad \Delta S^0 = -4 \text{ cal} \cdot \text{mol}^{-1} \text{K}^{-1}. \quad (11)$$

Although predicted curves 1 and 2 are clearly different, both parameter sets, (10) and (11), are fairly close numerically. This indicates that the experiments and the presented model are consistent with each other. Moreover, further refinement of the model parameters may be difficult due to a very sharp dependence of the LDL fraction  $c$  near the Widom line.

It should be noted that according to our model the LDL fraction at large temperatures tends to the non-vanishing constant value that disagrees with experimental points. It is a drawback of the model resulting from the linear approximation (6). Nevertheless, this fraction is small for correspondent choice of parameters such as (11).

**3. Discussion.** The analysis of the heat capacity and the LDL fraction measurements established the model parameters and predicted the temperature dependence of the dielectric constant for comparison with empirical data. The dielectric constant of the liquid is the sum of the LDL,  $\epsilon_{\text{LDL}}$  from Eq. (3), and the HDL,  $\epsilon_{\text{HDL}}$ , contribution, given by Debye–Onsager model:  $\epsilon_{\text{HDL}} = \epsilon_{\infty} + 2\pi n_0 d_0^2 (\epsilon_{\infty} + 2)^2 / (9T)$  [82]. Since the HDL fraction is  $1 - c$ ,  $\epsilon = c\epsilon_{\text{LDL}} + (1 - c)\epsilon_{\text{HDL}}$ , and so

$$\epsilon = \epsilon_{\infty} + \epsilon_{\infty} c(T) f(\tau) + [1 - c(T)] \frac{2\pi n_0 d_0^2}{9T} (\epsilon_{\infty} + 2)^2, \quad (12)$$

which can be compared to the recent measurements in nm-sized porous materials [42–44]. To achieve the stable liquid state at  $T \sim T_F$ , water samples were confined in polymerized silicate MCM-41 [83] with cylindrical pores of diameters  $D = 3.5$  nm. Though the nature of the confined water phase states has long been a source of controversy, recent studies show that thermodynamic properties of water in cavities larger than approximately 1 nm are essentially the same as in the bulk (see, for example, papers [84, 85] and references therein). The dielectric response of the sample was detected by the dielectric spectroscopy method at frequency range 25 Hz–1 MHz.

The results of the measurements and the theoretical predictions corresponding to the parameters set (10) and  $\epsilon_{\infty} = 4.7$  yield  $T_F = T_F^{\text{exp}} = 235$  K. These results are presented in Fig. 4. At temperatures well above the transition point,  $T > T_F, T_W$ , our model agrees with the

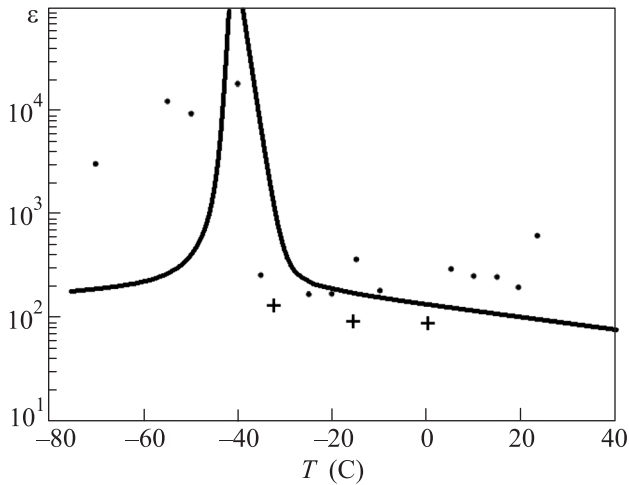


Fig. 4. Dielectric constant for bulk water versus temperature. Results of formulas (12), (10) are given by solid curve. Experimental results [42, 43] are presented by points, crosses correspond to the measurements [3]

experiment fairly well. The temperature dependence of the dielectric constant is much stronger than predicted by a simpler, single-component model [51]. Hence, the two-liquid phenomenology clearly improves the agreement with experimental results. The singularity of the dielectric constant is directly associated with the phase transition in the liquid water only, as no singularity was observed in experiments with another porous material with substantially larger pores, SBA-15 [44]. This also means that the effects observed in experiments with MCM-41 samples take place in a liquid water and are not a result of the freezing process. Below the transition point,  $T < T_F$ , the experiments paint a distinctly different picture. The temperature  $T_F$  may depend on the LDL cluster size and, therefore, we may face a “continuous set” of ferroelectric transitions in a multitude of LDL clusters as the temperature decreases. It leads to the observed large values of  $\epsilon$  at  $T < T_F$ .

Although we predict that FPT in LDL does lead to a dramatic increase of the dielectric constant near  $T_F$ , Eq. (2) shows that at small pressures near the phase transition,  $|\tau| \ll 1$ , the dipole-dipole interaction contribution to the Gibbs energy of the liquid is small,  $|\Delta G_P| \ll |\Delta G_L|$ . Therefore, FPT occurs at  $T \approx T_F$  in the background of the LLPT driven by the lattice rearrangements. Consequently, the influence of FPT on water properties at temperatures near the Widom line or higher (see Fig. 1) is negligible. A fair increase in the dielectric response of large water samples was also observed in the earlier experiments by Angel et al. [3]. We believe that the experimentalists measured mostly the third term of Eq. (12) and could have possibly missed

the FPT, described by the second term, by a few degrees. This means that the observation of the true singularity, and hence the evidence for FPT, have only become possible after the introduction of the novel nm-sized materials such as MCM pores.

Further away from the phase transition temperatures,  $|\tau| \sim 1$  we believe that  $|\Delta G_P| \sim |\Delta G_L|$  and therefore the lattice and the dipole-dipole interaction forces are equally important. The analogy between the ice 1h and LDL suggests that the energy of the dipole-dipole interactions released in the course of the FPT is thus transformed into the lattice rearrangements that occurs in FPT in ice. Therefore, it is reasonable to assume that, in reality, LLPT has a mixed nature and the liquid is probably in a ferro-electric phase below KP line.

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