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Is there a liquid-liquid phase transition in supercooled water?

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Abstract. – Previous studies of the structure of liquid water under pressure performed by neutron diffraction allowed us to establish two structural limits in liquid water. These two limits are closely connected to the two known forms of amorphous ice: the low-density amorphous ice (LDA) and the high-density amorphous ice (HDA). In the present paper, we propose some interpretation of our data in terms of a “two-level”-type model of water. This leads to show some evidence of a liquid-liquid phase transition in liquid supercooled water. The result looks in agreement with recent computer simulations that incorporate the two forms of amorphous ice.

One of the present challenging problems in the physics of liquid water is to give experimental evidence of the existence of a second critical point C' . This second critical point in low-temperature water is in addition to the known critical point C . Below the critical temperature T_C two fluid phases—a lower-density gas and a higher-density liquid—coexist. Above T_C these two states merge into a single “fluid phase” such that liquid and gas phases can be considered as polymorphs of the disordered fluid state. Therefore, polymorphism is not restricted to crystals [1]. Just as C separates a 1-fluid region above T_C from a 2-fluid region below T_C , C' separates a 1-liquid region above $T_{C'}$ from a 2-liquid region below $T_{C'}$. If the coexistence of two distinct liquids is common in multicomponent systems, it occurs also in pure, isotropic substances such as liquid crystals. Composition and molecular orientation are the respective order parameters of the transition. However, “liquid polymorphism” associated with a liquid-liquid phase transition is not commonly observed for pure, isotropic substances [1]. Nevertheless, such a behaviour was expected from abrupt changes in density and glass structures when changing pressure in SiO_2 [2], GeO_2 [3] and H_2O [4].

In the case of water, the polymorphism is indeed remarkable and apart from all the crystalline phases which are present in the phase diagram [5], one must add two amorphous solids, the low-density amorphous ice (LDA) and the high-density amorphous ice (HDA). The values of the density are 0.94 g/cm^3 for H_2O (1.04 g/cm^3 for D_2O) and 1.17 g/cm^3 for H_2O (1.30 g/cm^3 for D_2O), respectively. Mishima and collaborators [6] have discovered for the first time the high-density amorphous ice. Its microscopic structure has been studied both by X-ray [7] and neutron diffraction [8]. The pair correlation functions of the two forms of amorphous ice exhibit significant differences beyond the first nearest-neighbour distance (2.8 \AA). An appropriate description of the structure of the low-density form has been given in terms of a continuous random network model [9]. In this model the basic building unit is a water pentamer. This is equivalent to a description of the molecular arrangement in water by a continuous network of tetrahedrally coordinated H-bonds. In the case of high-density form, it is clear that the tetrahedrally coordinated patches are no longer present, either because the hydrogen bonds are broken or more likely because the hydrogen bond network is distorted. Moreover, we have been able to follow the transition between the high- and the low-density

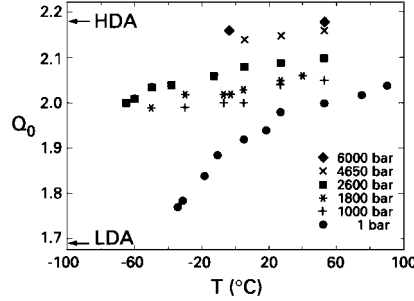


Fig. 1. – Evolution of the first peak position Q_0 of $S_M(Q)$ of D_2O vs. temperature at constant pressure. The values of Q_0 for LDA and HDA are indicated by the arrows.

forms, both by X-ray and neutron diffraction [7], [8]. We have shown that the pair correlation function of low-density amorphous ice obtained by heating high-density amorphous ice was nearly identical to those of amorphous ice prepared either by rapid cooling of water droplets on a cryoplate [10], or by vapour deposition onto substrates cooled at 77 K [11].

Recent computer molecular-dynamics simulations of the temperature-pressure (T - P) phase diagram of water have been performed [12]-[14] by using different effective pair potentials for liquid water. Results of the simulations indicate the presence, in the (T , P) phase diagram, of a first-order phase transition line separating two fluid phases, a low-density liquid (LDA) and a high-density liquid (HDA); this transition line terminates in a second critical point whose coordinates $T_{C'}$ and $P_{C'}$ are dependent on the chosen effective pair potentials of water.

The possibility of a second critical point has also been supported by two-level models for water [15], [16] and by lattice gas models [17]. The molecular-dynamics simulations as well as the two-level models of water tend to locate the second critical point in the deeply supercooled state, and below the homogeneous nucleation line T_H , as experimentally determined by Kanno and Angell [18]; that is to say, $T_{C'} \approx 200$ K, $P_{C'} \approx 500$ – 1000 bar from the simulations, $T_{C'} \approx 225$ K, $P_{C'} \approx 330$ bar from the two-state models.

How does one access experimentally this second critical point? This point must terminate the line of liquid-liquid phase transition for which the appropriate order parameter is the density. A convenient strategy involves exploring the system over a wide range of pressure and temperature. One relevant quantity to be connected with a change in density is the microscopic structure of the system. Recently, the microscopic structure of liquid D_2O has been investigated by neutron diffraction, in the stable and metastable regions of the phase diagram, at pressures up to 6000 bar and in a range of temperatures from 53 °C down to -65 °C [19], [20]. In order to study the deeply supercooled water, we made use of emulsions of D_2O in deuterated heptane, stabilized with sorbitan as surfactant [19]. In this paper, the microscopic structure of liquid water is re-examined on the basis of a two-level model as proposed in ref. [15] and [16]. The experimental data have been completed by calculating the pair correlation function $d_L(r, T, P)$ for a given temperature, at any pressure, using the derivative pressure function as defined in ref. [19]. Let us recall that the molecular structure factor is given by

$$S_M(Q) = D_M(Q) + f_1(Q), \quad (1)$$

where $D_M(Q)$ is the intermolecular contribution and $f_1(Q)$ the molecular form factor of water. It is to be noted that in the case of water, the functions $S_M(Q)$ and $D_M(Q)$ as well as their respective Fourier transforms $d(r)$ and $d_L(r)$ are composite functions. $d_L(r)$ is given by the expression

$$d_L(r) = 4\pi\rho_M r(g_L(r) - 1), \quad (2)$$

where ρ_M is the molecular density and $g_L(r)$ is the total pair correlation function with

$$g_L(r) = 0.489g_{OD}(r) + 0.421g_{DD}(r) + 0.090g_{OO}(r). \quad (3)$$

In these functions, the dominant contributions are due to the oxygen-deuterium and deuterium-deuterium pairs. Figure 1 gives the evolution of the main peak position Q_0 of the molecular structure factor $S_M(Q)$ as a function of temperature at various pressures. At normal pressure, a striking feature is the extremely strong temperature dependence of Q_0 when compared to higher pressures. It appears that Q_0 tends towards the value 1.69 \AA^{-1} which is characteristic of low-density amorphous ice [8]. At pressures up to 6000 bar, we observe some linear behaviour of the main peak position Q_0 as a function of temperature. Under a pressure of 6000 bar, when the temperature is increased up to 53°C , it appears that the main peak position of the structure factor of liquid water tends towards the value of 2.18 \AA^{-1} , which is characteristic for high-density amorphous ice [8]. This linear behaviour of the $Q_0(T)$ function is connected with some normal behaviour of water at low temperature when increasing pressure, and is in agreement with the thermodynamic and transport properties [21]. It appears that we have two limits in liquid water: LDA as the limit of deeply supercooled water (at normal pressure and low temperature) and HDA as that of liquid water at high pressure and temperature. This suggests that in a one-component liquid as liquid water, there exist two interconvertible species HDA and LDA whose respective concentrations α and $(1 - \alpha)$ are temperature and pressure dependent; $\alpha(T, P)$ ranges between 0 and 1. The value close to 0 means that the structure is close to LDA; the value equal to 1 means that the structure of liquid water is close to that of HDA. In this context, a description of liquid water in terms of a two-level type model [15], [16] looks appropriate. The relative molar Gibbs free energy ΔG of a two interconvertible species/nonideal solution model can be evaluated (see eq. (4) of ref. [16]). The conditions for the a/a transition in a liquid have been intuited from eq. (4). As stated in this paper, in addition to producing double minima of equal depth in the $\Delta G/RT$ vs. α plot at the a/a transition, it is required that the plot exhibits a maximum at the midpoint concentration $\alpha = 0.5$. The model contains four parameters, ΔGH° , ΔS° , ΔV° and W , that have been evaluated using recent results of Mishima [4] relative to the interconversion of LDA and HDA water due to pressure changes in a narrow temperature range ($135 \text{ K} \pm 5 \text{ K}$). On compression LDA H_2O transforms quite sharply into HDA H_2O at 3200 atm. On subsequent decompression the HDA H_2O transforms equally sharply back into LDA H_2O at 500 atm. In ref. [16], it is shown that the two thermodynamic states (135 K, 500 atm) and (135 K, 3200 atm) are points on the two spinodal lines of the LDA/HDA H_2O thermodynamic stability diagram. From eq. (4) of ref. [16], it has been shown that the pressure P_{aa} for the a/a transition at a given T is the mean of the two spinodal pressures. Hence at $T_{aa} = 135 \text{ K}$ the equilibrium LDA/HDA $\text{H}_2\text{O} \Rightarrow$ HDA H_2O a/a transition pressure is given by the mean value of pressures at points on the spinodal lines (500 atm and 3200 atm), namely $P_{aa} = 1850 \text{ atm}$. The $\Delta G/RT$ vs. α isobars for water at $T = 135 \text{ K}$ were calculated. The 1850 atm plot indicates an a/a transition at this pressure, with the characteristics as mentioned above, and in particular a maximum at the midpoint concentration $\alpha = 0.5$. The calculation of the T vs. specific volume equilibrium phase diagram for the a/a transition in water allowed to estimate other values of a/a transition pressures equal to 600 bar and 1200 bar, along the coexistence line.

On the basis of the model [16], the pair correlation function $d_L(r, T, P)$ of liquid water (D_2O) can be expressed in terms of a linear combination of the pair correlation functions of high-density and low-density amorphous ice assuming that the contribution due to the cross terms are negligible:

$$d_L(r, T, P) = \alpha(T, P)\{d_L^{\text{HDA}}(r, T, P)\} + (1 - \alpha(T, P))\{d_L^{\text{LDA}}(r, T, P)\}. \quad (4)$$

The fit of the expression (4) to the experimental data allows us to extract the $\alpha(T, P)$

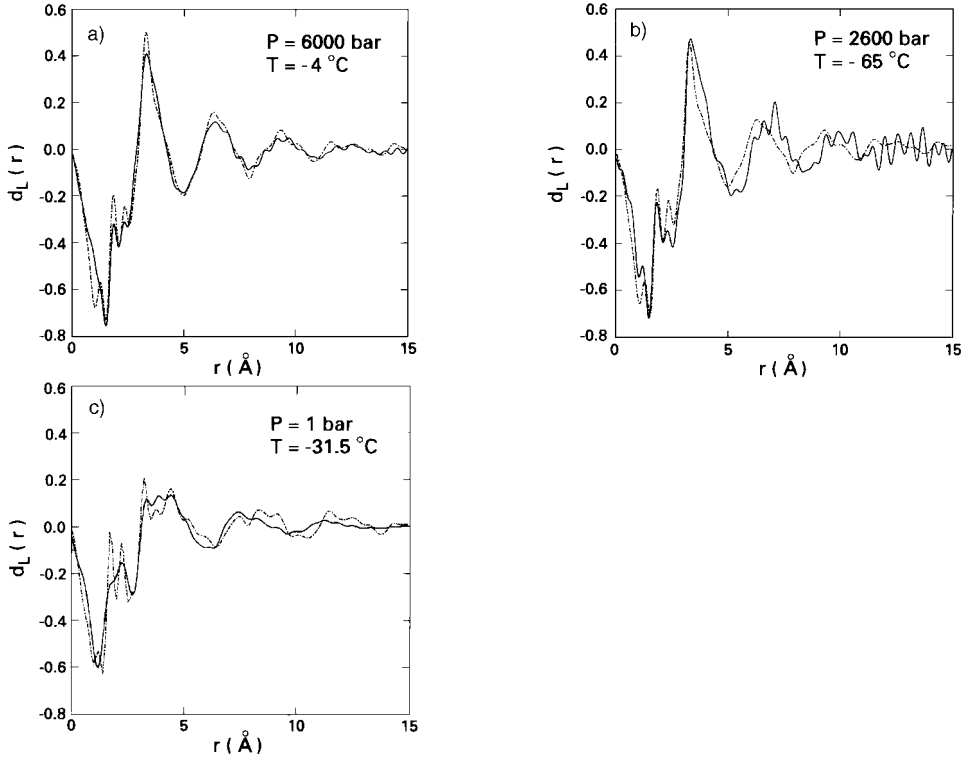


Fig. 2. – Pair correlation function $d_L(r)$ of D_2O at three thermodynamic states as compared with the result of the fit using eq. (4). Full line: experimental data; dotted line: result of the fit. Notice the close similarity between the state a) and HDA. State b) is close to HDA, in agreement with the transport properties [21]; the statistics is lower due to the nucleation problems.

concentration. Figures 2a), b), c) give the quality of the fit at three thermodynamic states. At high pressure (fig. 2a)), the value of $\alpha(T, P)$ is close to 1. The structure of the liquid is close to that of high-density amorphous ice which, similarly, occurs at 2600 bar and $-65^\circ C$ (fig. 2b)). At normal pressure, the value of the parameter drops to about 0.3 at $-31.5^\circ C$ which is the minimal temperature for which no nucleation occurs during the time of our experiment. Figure 2c) compares the result of the fit with the pair correlation function of deeply supercooled water and with that of low-density amorphous ice. In this case, the structure of the liquid phase is dominated by that of low-density amorphous ice.

Figure 3 gives the variation of the concentration $\alpha(T, P)$ as a function of temperature at various pressures. At high pressure, the value of $\alpha(T, P)$ is close to 1 and is weakly temperature dependent. This allows us to define a region of high-density liquid. As the pressure is decreased, the value of $\alpha(T, P)$ decreases as a function of temperature. At normal pressure, the concentration $\alpha(T, P)$ exhibits a marked temperature dependence and can be extrapolated to zero which corresponds to LDA. This limiting value equal to zero looks to be reached at some temperature close to the temperature of mechanical stability T_S ($-45^\circ C$ for H_2O , $-42^\circ C$ for D_2O) as established by Angell and Kanno [22].

From the above results, we expect to have some a/a liquid phase transition. Based on the thermodynamic considerations that the $\Delta G/RT$ vs. α plot at the a/a transition exhibits a maximum at the midpoint transition $\alpha = 0.5$, we have reported in fig. 3 the line $\alpha(T_{aa}, P_{aa}) = 0.5$. It has to be noticed that this line can only be intersected by the $\alpha(T, P)$ isobar curves corresponding to pressures less than 2000 bar. We obtained intercepts between the $\alpha(T, P_{aa})$

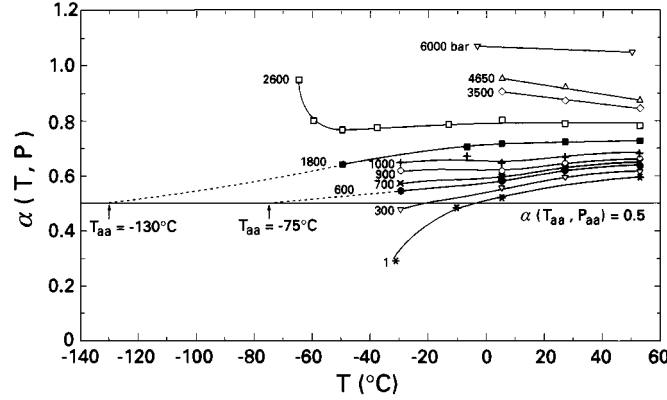


Fig. 3. – Evolution of $\alpha(T, P)$ vs. temperature at constant pressure. The curves $\alpha(T, P_{aa})$, with $P_{aa} = 600$ and 1800 bar, have been extrapolated at low temperature to intercept the line $\alpha(T_{aa}, P_{aa}) = 0.5$ (full line). The values of the corresponding T_{aa} are indicated by the arrows. The (T_{aa}, P_{aa}) points allow us to define the liquid-liquid transition line. At $300, 600, 700, 900$ and 3500 bar the $\alpha(T, P)$ curves have been deduced from the $d_L(r, T, P)$ as calculated using eq. (18) of ref. [19]. (The relative uncertainty on $\alpha(T, P)$ is about 5%.)

curves ($P_{aa} = 600, 1800$ bar) with the $\alpha(T_{aa}, P_{aa}) = 0.5$ line; we got some estimates (198 and 143 K) of the temperatures T_{aa} to be compared with the values 210 K and 135 K at close pressures P_{aa} of 600 and 1850 bar [16]. These intercepts are deduced from an extrapolation of the $\alpha(T, P_{aa})$ curves in a region located below the nucleation line T_H ; this region is difficult to be experimentally attained. In fact, at 1800 bar, it was not possible to go below -50 °C ($T_H = -67$ °C). In the (T, P) phase diagram of water (fig. 4), we have reported the thermodynamic states (T_{aa}, P_{aa}) with the inferred values of the temperatures T_{aa} , corresponding to the a/a transition as compared to those of Moynihan [16]. It has been possible to extrapolate the a/a transition line, at low temperature, to the HDA/LDA equilibrium transition line of Whalley *et al.* [23] estimated not for D_2O but for H_2O . We also reported the estimates of the (T, P) location of the new critical point C' as obtained respectively by molecular-dynamic simulations [12]–[14] and by the two-level-type models [15], [16].

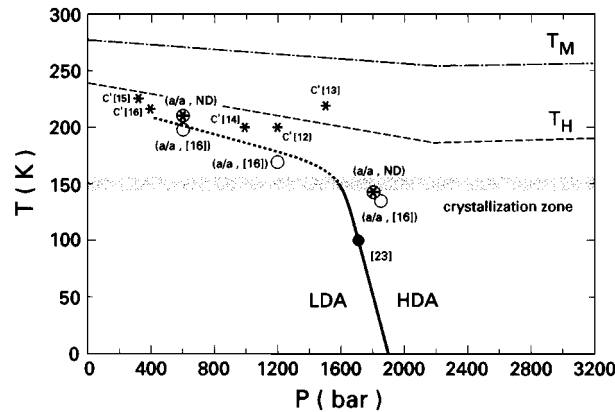


Fig. 4. – Phase diagram (T, P) of D_2O including the melting line T_M , the nucleation line T_H [22], the crystallization zone (grey part) and the possible transition line (dotted line). The (T_{aa}, P_{aa}) states are reported: from neutron data (a/a, ND), from ref. [16] (a/a, [16]). The estimates of the location of the new critical point have also been reported (asterisks).

In conclusion, firstly, this paper demonstrates that liquid polyamorphism can be observed by neutron diffraction in liquid water. We stress that two distinct liquid “phases” are present in liquid water. The two “phases” (HDA and LDA) have the same molecular structure but differ in their thermodynamic properties and their local structures. Secondly, using a two-level model, it has been possible to reproduce the experimental $d_L(r, T, P)$ data and to point out the possibility of an a/a liquid phase transition which occurs in supercooled water. However, our results do not allow us to demonstrate the existence of a new critical point. If this new critical point exists and if the compressibility diverges as suggested by lattice model calculations [17], this must give rise to density fluctuations that increase when approaching the critical point. Small-angle neutron and/or X-ray scattering experiments could be a possible means to demonstrate the existence of a second critical point if the transition is associated to a large increase in density fluctuations. This phenomenon is currently observed close to the liquid-gas critical point and has been observed by neutron scattering experiments on supercritical water [24].

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REFERENCES

- [1] POOLE P. H., GRANDE T., ANGELL C. A. and McMILLAN P. F., *Science*, **275** (1997) 322.
- [2] GRIMSDITCH M., *Phys. Rev. Lett.*, **52** (1984) 2379.
- [3] SMITH K. H., SHERO E., CHIZMESHY A. and WOLF G. H., *J. Chem. Phys.*, **102** (1995) 6851.
- [4] MISHIMA O., *J. Chem. Phys.*, **100** (1994) 5910.
- [5] HOBBS P. V., in *Ice Physics* (Clarendon, Oxford) 1974.
- [6] MISHIMA O., CALVERT L. D. and WHALLEY E., *Nature*, **314** (1985) 76.
- [7] BIZID A., BOSIO L., DEFRAIN A. and OUMEZZINE M., *J. Chem. Phys.*, **87** (1987) 2225.
- [8] BELLISSENT-FUNEL M.-C., TEIXEIRA J. and BOSIO L., *J. Chem. Phys.*, **87** (1987) 2231.
- [9] BOUTRON P. and ALBEN R., *J. Chem. Phys.*, **62** (1975) 4848.
- [10] MAYER E., *Cryo. Lett.*, **9** (1988) 66.
- [11] NARTEN A. H., VENKATESH C. G. and RICE S. A., *J. Chem. Phys.*, **64** (1976) 1106.
- [12] POOLE P. H., ESSMANN U., SCIORTINO F. and STANLEY H. E., *Phys. Rev. E*, **48** (1993) 4605.
- [13] HARRINGTON S. T., ZHANG R., POOLE P. H., SCIORTINO F. and STANLEY H. E., *Phys. Rev. Lett.*, **78** (1997) 2409.
- [14] TANAKA H., *J. Chem. Phys.*, **105** (1996) 5099.
- [15] PONYATOVSKII E. G., SINITSYN V. V. and POZDNYAKOVA T. A., *JETP Lett.*, **60** (1994) 360.
- [16] MOYNIHAN C. T., *Mat. Res. Soc. Symp. Proc.*, **455** (1997) 411.
- [17] ROBERTS C. J. and DE BENEDETTI P. G., *J. Chem. Phys.*, **105** (1996) 658.
- [18] KANNO H. and ANGELL C. A., *J. Chem. Phys.*, **73** (1980) 1940.
- [19] BELLISSENT-FUNEL M.-C. and BOSIO L., *J. Chem. Phys.*, **102** (1995) 3727.
- [20] BELLISSENT-FUNEL M.-C., in *Physical Chemistry of Aqueous Systems*, edited by H. J. WHITE JR., J. V. SENGERS, D. B. NEUMANN and J. C. BELLOWS (Begell House, New York) 1995, p. 332.
- [21] PRIELMEIER X., LANG E. W., SPEEDY R. J. and LUDEMANN H. D., *Ber. Bunsenges. Phys. Chem.*, **92** (1988) 1111.
- [22] ANGELL C. A. and KANNO H., *Science*, **193** (1976) 1121.
- [23] WHALLEY E., KLUG D. D. and HANDA Y. P., *Nature*, **342** (1989) 782.
- [24] BELLISSENT-FUNEL M.-C., TASSAING T., ZAO H., BEYSENS D., GUILLOT B. and GUISSANI Y., *J. Chem. Phys.*, **107** (1997) 2942.