The liquid water polymorphism

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The report of Nilsson and coworkers in this issue of PNAS (1) is an important step toward understanding the mysterious properties of water.

Water is certainly the most essential of all molecules in nature. Understanding its role in many aspects of life represents the most challenging problem in science. Despite its importance and ubiquity on the earth and despite many centuries of research, water is certainly the most complex liquid, being characterized by counterintuitive properties ("the 64 anomalies of water"). Unlike most liquids, water becomes most dense not when it is coldest but at 4 °C.

Other water anomalies include thermodynamic properties such as isothermal compressibility K_T, isobaric heat capacity C_P, and thermal expansion coefficient α_P (2–4). In particular, these functions, extrapolated from their values in water's metastable supercooled phase (located between its homogeneous nucleation temperature, $T_H = 231$ K, and the melting temperature, $T_M = 273$ K), all appear to diverge at a singular temperature ($T_S \simeq 228$ K). Water can also exist in the liquid form at extremely low temperatures as a glass (3) below the glass transition temperature $T_g \sim 130$ K. Just above T_g, glassy water transforms into a highly viscous fluid and finally crystallizes at $T_X = 150$ K (2). The region between T_X and T_H is a region where bulk liquid water cannot be studied, the so-called no-man's land (4).

Among the many theoretical approaches (5–7) developed to explain water properties, the liquid–liquid critical point (LLCP) hypothesis (7) has received the most substantial support from various experimental (8, 9) and theoretical studies (10, 11). The explanation stems from the role played by the hydrogen bond (HB) interaction among water molecules. More precisely, the HB governs the overall structure and the dynamics of water, giving rise, on decreasing T, to a clustering process for which an open tetrahedrally coordinated HB network gradually develops. The LLCP hypothesis is based on an argument advocating the continuation of the local structure of the liquid water into its amorphous solid phases. Amorphous water is known to display polymorphism: it has a low-density amorphous (LDA) and also a high-density amorphous (HDA) solid phase (12, 13) that can be made below T_g and can be transformed from one to the other by tuning pressure.
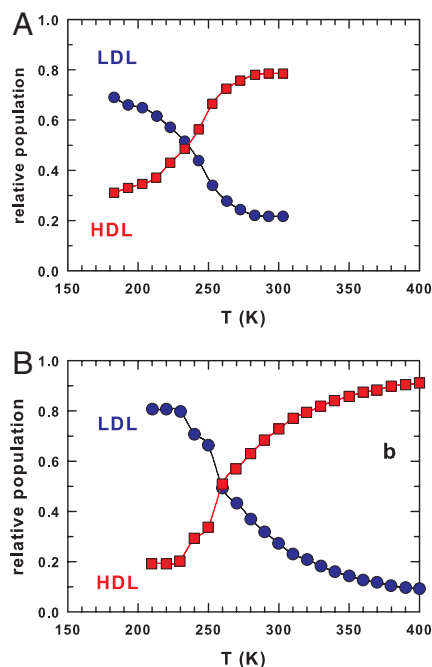

Fig. 1. The populations of the two liquid local water structures. (*A*) The populations of the low-density liquid (LDL) and the high-density liquid (HDL) water phases measured in confined geometry by means of light spectroscopy (18). (*B*) The same populations obtained in bulk water by means of a molecular dynamics simulation for the TIP5P water potential (21).

It is therefore possible that the liquid state is a mixture of the two corresponding liquid local structures, one corresponding to a low-density liquid (LDL) and the other to a high-density liquid (HDL) (7). The difference between the two liquids lies in their local structures: in the HDL, the local tetrahedrally coordinated HB structure is not fully developed, whereas in the LDL, a more open, locally "ice-like" HB network is realized. In this view, water anomalies are a reflection of the "competition" between these two local liquid forms. An important feature of the LLCP scenario is the presence of a Widom line $T_W(P)$, in the T–P phase diagram. The Widom line is the locus of the correlation length maxima in the one phase region beyond the LLCP, where thermodynamic response functions take their maximum values (14, 15). It separates water with more HDL-like local structures at high temperatures from water with more LDL-like local structures at low temperatures. The presence of the Widom line influences quantities such as density, viscosity, relaxation times, and the self-diffusion coefficient, and it offers an explanation of the anomalies in quantities such as specific heat or isothermal compressibility.

To clarify these aspects one would like to observe two water liquid phases inside the no-man's land. By confining water in nanoporous structures so narrow that the liquid cannot freeze, experiments recently have been made by using neutron and Raman scattering and NMR spectroscopy (9, 16–20). (See Fig. 1.) In particular, in one of these studies (9) the Widom line was identified in the T–P phase diagram, whereas in another one (18) clear signs of the two types, LDL and HDL, of water inside the supercooled region are reported. These findings, however, are open to the criticisms that the behavior of the water may have been altered by the silica pore surfaces or that water confined in very narrow nanopores has a structure different from that of bulk water.

Very recently (21), by using the electron spin resonance technique, water confined within ice itself has been studied. The mobility of water molecules within tiny pockets of liquid trapped between ice crystallites has been measured down to 90 K. However, the experiment does not measure water dynamics directly, but rather the motion of an organic molecule (TEMPOL, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) is used as a sort of probe diffusing in water, thus sensitive to the water viscosity. Inside the interval $130 < T < 273$ K, two motions of the probe reflecting the presence of two distinct types of water are observed: the more viscous LDL form and the more fluid HDL.

The report of Nilsson and coworkers (1) offers key experimental evidence on the long-standing issue of the existence of the two liquid phases in bulk water. These authors demonstrate that the density difference contrast measured in small-angle X-ray scattering (SAXS) is due to large length scale fluctuations between tetrahedral and hydrogen-bond distorted structures related to the low- and high-density water, respectively. Directly from SAXS and spectroscopic information it is in-
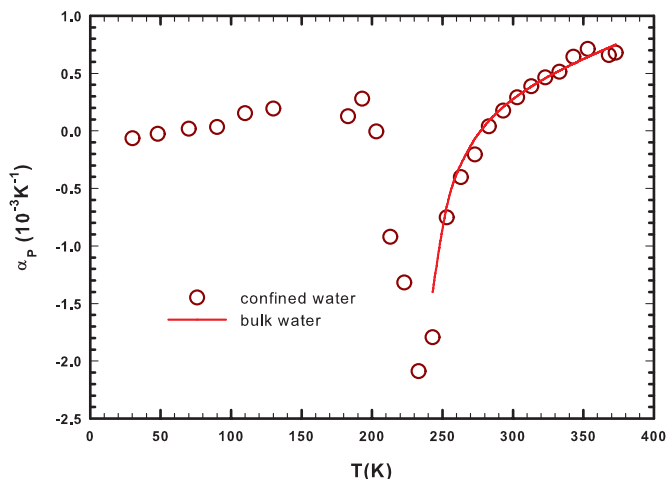
Fig. 2. The thermal expansion coefficient α_ρ measured in confined water. The red line is the same quantity obtained from the bulk water density.

ferred that the water structure is due to a temperature-dependent fluctuating equilibrium between the two types of local structure driven by enthalpy minimization (HB tetrahedral-like network) and maximizing entropy (disorder and distorted HB). In addition, differences in these HB structures, typical of the deeply supercooled regime, remain in bulk water even at ambient condition.

The importance of the physical scenario presented by Nilsson and coworkers (1) is twofold. It confirms the existence of water polymorphism and, being defined on density fluctuations concepts, also confirms and highlights the role of the physical quantities related with the concept of the Widom line, demonstrating that the corresponding temperature $T_W(P)$ marks, on decreasing T at constant pressure, the crossover from a predominance of an

"HDL-like" local structure to a predominance of an "LDL-like" local structure.

It must be stressed that the entire picture present in ref. 1 is consistant with the findings on the dynamical properties of water obtained in previous experiments on confined water (9, 16–20) and in molecular dynamics simulation studies in bulk (14, 15) and also supports the suggestion that the explanation of some water anomalies can be obtained by considering that $T_W(P)$ is the locus of the maxima in the thermodynamic response functions. In particular, these properties, just on crossing of the Widom line, $T_W(P) \simeq 225$ K, are as follows:

(*i*) a fragile-to-strong crossover (9, 14–16),
(*ii*) the violation of the Stokes–Einstein relation (17, 22),

(*iii*) the observation of the predominance of LDL on the HDL local structure (18, 21),
(*iv*) local maxima in the configurational specific heat (23) and in the absolute value of the thermal expansion coefficient (19, 20).

Scattering methods show the existence of a density minimum in both D_2O and H_2O, at about 200 K (19, 20). The recent molecular dynamics study on the appearance of the fractional Stokes–Einstein relation in water shows that this phenomenon arises from a specific change in the local water structure and confirms that, as clearly stated in the study by Nilsson et al. (1), the LDL-like local structure persists also at ambient conditions (21).

In the context of the water anomalies, the dynamical scenario dominated by large-scale fluctuations in the water correlation functions, as proposed by Nilsson and coworkers (1), can be the clue of their explanation. NMR experiments show a maximum in the water configurational heat capacity just at T_W, whereas the density (characterized by the well-known maximum at 277 K and a minimum at about 200 K) has at this temperature (225 K) its flex point reflecting the change in population between the two liquid water phases. Furthermore, from the measured densities, we find that a quantity related to the cross-correlation between the entropy and volume fluctuations, $\alpha_\rho = -(\partial \ln \rho/\partial T)_P = \langle \delta S \delta V \rangle / k_B T V$ shows a well-defined minimum at T_W (Fig. 2). Thus, the thermal behavior of the two quantities, C_P and $|\alpha_\rho|$, explains water anomalies, showing that the thermodynamic response functions are characterized by large-scale fluctuations rather than diverging behaviors.

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