

Role of hydrogen-bond cooperativity and free-volume fluctuations in the non-Arrhenius behavior of water self-diffusion: A continuity-of-states model

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Some thermodynamic and transport properties of normal and supercooled water have been interpreted in the framework of a dynamic extension of the polychromatic percolation model in which both the recently reported evidence for a temperature-dependent H-bond cooperativity and free-volume fluctuations within the percolative patches are included. The proposed model, which allowed us to fit the experimental self-diffusion data as a function of the temperature to an accuracy comparable to that obtained by a power law, is consistent with the existence of a continuity of states between liquid and solid phases, rather than being indicative of the presence of singularities in the supercooled region.

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INTRODUCTION

Many of the static and dynamic properties of liquid water present an anomalous behavior, which is particularly enhanced in the supercooled region. One of the most intriguing questions regarding water is, how should liquid water behave below the freezing point if nucleation phenomena are somehow prevented? There exist essentially two possibilities: The first is that the water properties retain the same trend they have just below the freezing point and, consequently, a number of them undergo a divergence at the temperature $T_S = -45^\circ\text{C}$ [1-6]; the second is that these properties change their trend below the lowest temperature experimentally reached up to now and then connect with the properties of ice [7-11].

The principal evidence supporting the existence of a singularity at the temperature T_S is based on the observation of a power-law temperature dependence of a number of water properties which seem to diverge or go to zero at the same temperature [1,2]. Among these, the transport properties deserve particular attention since no normal-like background corrections are required [1-6]. Actually, Prielmeier *et al.* [6] have shown that, in the low and moderate regime of pressure, the power law is superior to the Vogel-Fulker law in the interpretation of the strong non-Arrhenius behavior of the water self-diffusion coefficient D . Moreover, they have connected the temperature T_S to the Speedy's mechanical stability limit conjecture, which assumes a continuous spinodal line extending from the critical point to the supercooled region [3-6]. This spinodal line, which is characterized by the condition $(\partial P/\partial V)_T = 0$, should change direction twice corresponding to the two intersection points with the maximum density curve.

The most remarkable consequence of the possible ex-

istence of a spinodal line is that a continuity of states between the supercooled liquid and the solid phase cannot exist. In fact, if the possibility of a change in the trend of water properties below the freezing point is disregarded, the extrapolation of the heat-capacity (C_p) data predict that no sufficient entropy should be available in order that thermodynamic states of liquid and solid phases can be connected [10]. Moreover, if a power-law temperature dependence is assumed for C_p [1,3,4], there should be an interval of temperatures just above T_S in which the supercooled liquid is much more ordered than ice, contradicting the third law of thermodynamics (the Kauzmann paradox).

On the other hand, some microscopic models for liquid water do not predict any singularity [7,10-12]; the anomalous behavior of the liquid properties arises from some peculiar characteristics of the H-bond network whose structure is, in turn, determined by the high directionality, the intermediate strength, and the cooperativity of the H bonds. Due to the charge distribution geometry, each water molecule should be limited to form a maximum of four linear H bonds (LHB); therefore, five different water species can be considered on the basis of the number of LHB's in which each molecule is engaged (from 0 to 4). Moreover, owing to the H-bond cooperativity, bonds are not made or broken singly but several at a time; thus short-lived clusters of highly bonded molecules are created (flickering clusters), the formation and dissolution of these clusters being governed by local energy fluctuations [12,13]. Quite recently, several forms of cooperativity have been singled out (polarization dependent [12], statistical [7], geometric [14], and stereodynamic [15]).

One of the most interesting consequences of the statistical correlation is that the cluster aggregation occurs selectively between water molecules having the same number of formed H bonds so that homogeneous microregions (patches) are created [7]. It should be noted that such a type of cooperativity is also effective in a ran-

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dom H-bond network. If the H bonds are assumed to be randomly distributed, the water molecules are binomially distributed among the five species; however, quite recently, significant deviations from such a binomial distribution have been inferred from molecular-dynamics simulations, indicating that other cooperative phenomena are operative together with the statistical correlation [16]. The final effect is the creation of cooperative patches in which collective motions, similar to those which are present in ice and recently observed by Raman-scattering spectroscopy, can take place [8–10,17].

In the present work we should stress the role of the cooperativity and of the free-volume fluctuations in the non-Arrhenius behavior of normal- and supercooled-water self-diffusion coefficients and show that the apparent divergence of some thermodynamic properties is consistent with the existence of a continuity of states between the liquid and the solid phase if the H-bond cooperativity is taken into account.

In particular, we consider water as described by five quantumlike energy levels corresponding to each of the five water species and admit a cooperative mechanism for the transitions from one level to another. We assume an environment-dependent probability of forming an H bond and obtain the water fraction distribution among the five species by solving the appropriate five-level master equation. The resulting temperature-dependent water fraction distribution is compared with the experimental density (δ) and thermal expansion coefficient (α) data, thus obtaining some relevant H-bond network parameters which, on the other hand, are able to interpret the experimental isothermal compressibility (K_T) data. The water self-diffusion coefficient is evaluated as the mean, weighed over the equilibrium distribution water fractions, of the diffusion coefficients $D_j(T)$ relative to each species which, in turn, are calculated by taking into account the energy and density fluctuations within unlike patches [13,18–20]. The proposed model is able to fit the experimental NMR water self-diffusion data to a goodness comparable with that obtained by fitting the same set of data with a power law. The results suggest the possible existence of a continuity of states between the supercooled liquid and the ice phase rather than being indicative of a spinodal behavior or of the existence of a critical point [21].

EXPERIMENT

Self-diffusion coefficients were measured, by a homemade 10-MHz low-resolution (spin-echo) NMR spectrometer [22], with the static magnetic-field-gradient technique, by comparing the zero-gradient spin-echo amplitude with the amplitude of the echo at different field-gradient values. The field gradient was calibrated by using pure water at 25 °C as a reference [23]. Temperature control was performed by inserting the sample into a nitrogen flux at a predetermined temperature which was taken constant by an ON–OFF heating controller. Water samples were prepared with a Milli-Q system and sealed in the test tube by parafilm and silicone glue. Spin-echo curves, as a function of the square of the gradient intensi-

ty, were fitted by a single exponential least-squares-fitted routine. The time of observation of the diffusion process, i.e., the interval in which the molecules are exposed to the gradient field, was taken constant (18 ms) in the overall temperature range.

WATER SELF-DIFFUSION

As for the majority of the water properties, the characteristic feature of the self-diffusion coefficient can be traced back to the peculiar structure and dynamics of the H-bond network. Due to the different environments in which a water molecule can be found, according to the number of H bonds in which it is engaged, the diffusional phenomena turn out to be the superposition of different behaviors which range from the vibrational-like behavior of the four-bonded molecules to the rototranslational motion of the zero-bonded ones. Recently, Bertolini *et al.* [24,25] have studied the H-bond dynamics taking into account the thermal-bath-induced transitions between the five water species and have found the self-diffusion coefficient (D) to be expressed by the mean, weighed over the equilibrium distribution of the water fractions, of the self-diffusion coefficient relative to each of the five water environments:

$$D(T) = \sum_{j=0}^4 D_j(T) f_j(T), \quad (1)$$

$D_j(T)$ and $f_j(T)$ being, respectively, the temperature-dependent diffusion coefficient and the fraction of the water molecules belonging to the j th species. An attempt to interpret the experimental data by means of Eq. (1) should then require knowledge of (i) the distribution of the water species, (ii) its temperature dependence, and (iii) the diffusion coefficients for each of the five water environments.

WATER FRACTION DISTRIBUTION AND H-BOND COOPERATIVITY

In order to evaluate the fractions $f_j(T,P)$, let us assume that water is described by five quantumlike states corresponding to the five water species [24–26]. If the simultaneous forming and breaking of more than one H bond (i.e., the transitions from nonadjacent energy levels) are statistically negligible events, the time evolution of the water molecule fraction belonging to the j th species is described by the following master equation:

$$\begin{aligned} \frac{d}{dt} f_0 &= k_{10} f_1 - k_{01} f_0, \\ \frac{d}{dt} f_1 &= k_{01} f_0 + k_{21} f_2 - (k_{10} + k_{12}) f_1, \\ \frac{d}{dt} f_2 &= k_{12} f_1 + k_{32} f_3 - (k_{23} + k_{21}) f_2, \\ \frac{d}{dt} f_3 &= k_{23} f_2 + k_{43} f_4 - (k_{32} + k_{34}) f_3, \\ \frac{d}{dt} f_4 &= k_{34} f_3 - k_{43} f_4, \end{aligned} \quad (2)$$

where k_{ij} is the transition rate from state i to state j . The equilibrium solution of Eq. (2), at a fixed temperature and pressure, is given by the recursive formula

$$f_{j+1}(T,P) = \frac{k_{j,(j+1)}(T,P)}{k_{(j+1),j}(T,P)} f_j(T,P), \quad j=0,1,2,3 \quad (3)$$

the value of $f_0(T,P)$ being calculated by the normalization condition $\sum_{j=0}^4 f_j(T,P) = 1$. By introducing the probability $p_j(T,P)$ that a water molecule in state j can form an H bond, Eq. (3) becomes

$$f_{j+1}(T,P) = \frac{(4-j)p_j(T,P)}{(j+1)[1-p_j(T,P)]} f_j(T,P), \quad j=0,1,2,3. \quad (4)$$

If the H-bond breaking and forming are assumed as statistically independent events, the probability of finding an H bond intact does not depend on the particular environment of the tagged molecule ($p_j = p_b$ for each j), and the equilibrium solution of the master equation is the binomial distribution [24,25]. Nevertheless, from molecular-dynamics simulation data it has been argued that the H-bond lifetime is strongly coupled to the environment of the linked molecule, the bonds which connect the four H-bonded molecules being the longest living [16,20]. Therefore, the probability p_j , which is directly related to the H-bond lifetime [24,27], has to be considered environment dependent and this would result in a nonrandom distribution of the H bonds with a consequent deviation from the binomial distribution for the water fractions. The correlation in the H-bond distribution would favor the spatial bond condensation [8,9,16,28] and induce the formation of water patches beyond the mere statistical effect [7]. At low temperatures, patches with four H bonds increase in size and number, allowing the system to undergo some collective motions, similar to those present in ice and recently observed by Raman-scattering spectroscopy [8,9]. Moreover, by increasing the concentration of the four H-bonded molecules, the probability for a water molecule of being surrounded by stable molecules increases and the formation of an additional H bond becomes more probable. The probability that a three-bonded molecule forms a fourth bond would result as higher the greater the concentration of the four-bonded molecules which, in turn, depends on such a probability. Such a cooperative mechanism which is, of course, limited by the thermal energy is then enhanced in the low-temperature region [2,8,9]. Similarly, at high temperature the creation of patches of nonbonded water molecules occurs. It should then be expected that the cooperativity would mainly affect the probability of forming an H bond in the zero- and four-H-bonded water patches, which are the most populated in the superheated and supercooled regions, respectively, and where most of the water anomalies are observed [2]. Accordingly, to take into account this H-bond cooperativity, we introduce a population-dependent perturbation in the probability of forming an H bond in the zeroth and fourth water species, whereas the remaining ones depend only on temperature and pressure:

$$\begin{aligned} p_0(T,P) &= p_{b_0}(T,P) - \lambda(P)f_0(T,P), \\ p_1(T,P) &= p_{b_1}(T,P), \\ p_2(T,P) &= p_{b_2}(T,P), \\ p_3(T,P) &= p_{b_3}(T,P) + \mu(P)f_4(T,P), \end{aligned} \quad (5)$$

$\lambda(P)$ and $\mu(P)$ being positive functions which measure the degree of cooperativity of the system and $p_{bj}(T,P)$ the probability of finding an H bond intact under the hypothesis of uncorrelated H bonds.

If we restrict our discussion to the case of the atmospheric pressure, $\lambda(P)$ and $\mu(P)$ are constants and $p_{bj}(T,P) = p_b(T)$. Therefore, by introducing Eq. (5) into Eq. (4) and by solving with respect to f_0 , we have

$$\begin{aligned} f_1 &= \frac{4(p_b - \lambda f_0)f_0}{(q + \lambda f_0)}, \\ f_2 &= \frac{6p_b(p_b - \lambda f_0)f_0}{q(q + \lambda f_0)}, \\ f_3 &= \frac{4p_b^2(p_b - \lambda f_0)f_0}{q^2(q + \lambda f_0)}, \\ f_4 &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}, \end{aligned} \quad (6)$$

where

$$\begin{aligned} q &= 1 - p_b, \\ a &= \mu q^2(q + \lambda f_0), \\ b &= \mu p_b^2(p_b - \mu f_0)f_0 - q^3(q + \lambda f_0), \\ c &= p_b^3(p_b - \lambda f_0)f_0. \end{aligned}$$

The use of the normalization condition $\sum_{j=0}^4 f_j = 1$ gives the following equation for f_0 :

$$\begin{aligned} (A^2 - K_1)f_0^4 + (2AB - K_2)f_0^3 + (B^2 + 2AC - K_3)f_0^2 \\ + (2BC - K_4)f_0 + D = 0, \end{aligned} \quad (7)$$

where

$$\begin{aligned} A &= -\mu\lambda(p_b^2 + 6), \\ B &= 2\mu(1 + p_b)(1 + p_b^2) - \mu p_b^3 + \lambda q^3 - 2\mu\lambda q^2, \\ C &= q^4 - 2\mu q^3, \\ D &= 4\mu q^6(\mu - q), \\ K_1 &= \lambda^2 \mu^2 p_b^4, \\ K_2 &= 2\lambda^2 \mu q^2 p_b^2(1 + p_b) - 2\lambda \mu^2 p_b^5, \\ K_3 &= \mu^2 p_b^6 + \lambda^2 q^6 + 2\mu\lambda q^2 p_b^2(1 + p_b)(1 - 2p_b), \\ K_4 &= 2q^3[\lambda q^4 - \mu p_b^3(1 + p_b)]. \end{aligned}$$

To avoid the burden of notation in the above formulas, the explicit dependence on the temperature has not been reported.

Equation (7) is solved numerically, for each value of its

coefficients, in the interval $0 \leq f_0 \leq 1$, where a single solution is always found except for the right end point of the interval, where two solutions exist.

**THE TEMPERATURE DEPENDENCE
OF THE WATER FRACTION
DISTRIBUTION: DENSITY, THERMAL EXPANSION
AND ISOTHERMAL COMPRESSIBILITY**

In the preceding section we have expressed the equilibrium distribution of the water fractions in terms of the probability p_b , so that the temperature dependence of f_j derives exclusively from such a probability. Before any expression is worked out for $p_b(T)$, some explanation should be made.

The use of five energy levels is a simplification; in fact, such a description of liquid water takes into account only the H bonds, whereas the van der Waals interactions are also present. In this connection, it should be considered that the zero-H-bond energy level is not the limit of the energy spectrum but many other states, with higher energy, exist; these are related to the water vapor and dissociated liquid phases which are dominated by the van der Waals forces. While, due to the smaller intensity of the van der Waals interaction with respect to the H-bond interaction, the five-level description is a good approximation to estimate the water fraction distribution in the liquid phase, the determination of its temperature dependence requires some consideration of the overall energy spectrum. From a statistical-mechanics point of view, the zero-H-bond energy level can be considered as the ground state with respect to the vapor-liquid condensation process: Under the action of the van der Waals forces, the vapor molecules condensate in a "dissociated" liquid phase, in which all the molecules are not H bonded, at a temperature T_c . On the other hand, the four-H-bond energy level can be considered as the ground state for the liquid-solid condensation and then is totally occupied as solidification occurs at the temperature T_0 . On the basis of these considerations, the probability $p_b(T)$ cannot be expressed in terms of a single Boltzmann exponential, but its form has to satisfy the following conditions:

$$\lim_{T \rightarrow T_0} p_b(T) = 1 \quad (\text{ice}),$$

$$\lim_{T \rightarrow T_c} p_b(T) = 0 \quad (\text{dissociated liquid}).$$

A simple expression containing exponential functions, as required by activated processes, which satisfy the above-mentioned conditions could be

$$p_b(T) = 1 - \exp \left[\frac{-E(T_c - T)}{R(T_c - T_0)(T - T_0)} \right], \quad (8)$$

E being a parameter that is in some way related to the average activation energy (to work out an exact relationship between E and the activation energy barrier, knowledge of the partition function of the system is necessary).

By introducing Eq. (8) into Eqs. (6) and (7), the expres-

sions for the water fractions are obtained as a function of the temperature. However, these expressions still depend on the unknown parameters λ , μ , T_c , T_0 , and E . Therefore, in order to evaluate $f_j(T)$, we need to know to which extent the system is cooperative and how much energy is necessary to activate the H-bond network restructuring. A physically sound way to extract this information would be to compare our master-equation solution with some reliable experimental data. For this purpose, the density $\delta(T)$ and thermal expansion $\alpha(T)$ data are the best candidates since these thermodynamic quantities are simply related to $f_j(T)$, and a large amount of good precision experimental data exist in a wide range of temperatures [29,30]. In fact, the water density and thermal expansion coefficient, for a 1-g water sample, are, respectively,

$$\delta(T) = \frac{1}{\sum_{j=0}^4 V_j(T) f_j(T)}, \quad (9)$$

$$\alpha(T) = - \frac{\partial \ln[\delta(T)]}{\partial T} = \frac{\sum_{j=0}^4 \left[V_j(T) \frac{\partial}{\partial T} f_j(T) + f_j(T) \frac{\partial}{\partial T} V_j(T) \right]}{\sum_{j=0}^4 V_j(T) f_j(T)}, \quad (10)$$

where $V_j(T)$ is the volume of the molecules belonging to the j th species, which turns out to be larger the higher the number of H bonds in which the molecule is engaged [7,16,31].

The volume of the water molecules with four H bonds can be estimated from the ice density [25] and the remaining water fraction volumes can be assumed to be linear with the temperature but, due to the smaller binding energy, a square term should be added for the non-bonded fraction:

$$\begin{aligned} V_0(T) &= V_0 [1 + \alpha_0(T - 273) + \beta_0(T - 273)^2], \\ V_j(T) &= V_j [1 + \alpha_j(T - 273)], \quad j=1,2,3 \\ V_4(T) &= 1/\delta_{\text{ice}}(T). \end{aligned} \quad (11)$$

The temperature derivatives of the water fractions $f_j(T)$ have been evaluated starting from Eq. (4), as reported in the details in the Appendix, while the derivatives of the volumes are simply calculated from Eq. (11).

To minimize the correlation between the parameters, we have fitted simultaneously, by a simulated annealing Monte Carlo algorithm [32], both the density and the thermal expansion coefficient data [29,30] by means of Eqs. (9) and (10), respectively.

Figures 1 and 2 show the best-fit curves for $\delta(T)$ and $\alpha(T)$, respectively, the value of the fit parameters being reported in Table I. The agreement with the experimental data is excellent, as indicated also by the low value of the fit standard deviations reported in the last two lines of Table I. The corresponding water fraction distributions have been plotted, as a function of the temperature, and are shown in Fig. 3, together with the relative binomial

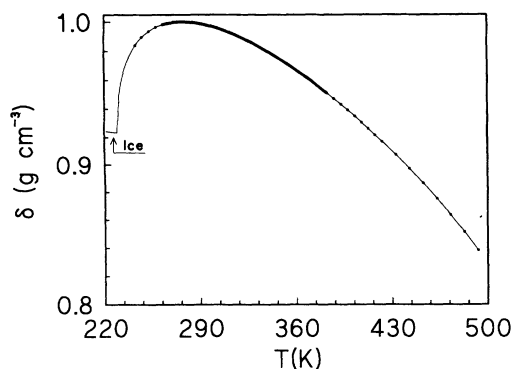


FIG. 1. Water density as a function of temperature. The solid line represents the best fit, by Eq. (9), of the literature data. The extrapolated fitting curve falls in with the ice density line at the temperature T_i (see the text).

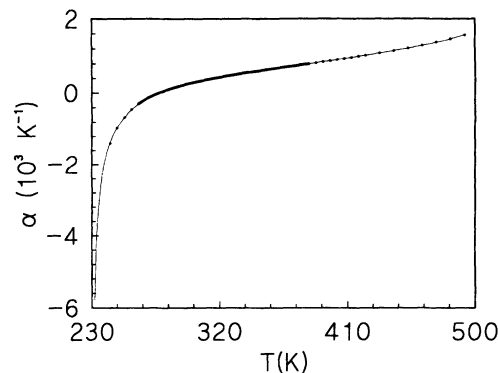


FIG. 2. Water thermal expansion coefficient as a function of temperature. The solid line represents the best fit, by Eq. (10), of the literature data.

distribution for a comparison. As the temperature is lowered, the fraction of four-H-bonded molecules, which are the most sensitive to cooperativity effects, undergoes a faster increase with respect to the binomial one, in qualitative agreement with the molecular-dynamics-simulation data [16]. A similar behavior is also observed for the zero-H-bond fraction at high temperature.

In Fig. 4 the probability $p_b(T)$ is shown and compared with the values obtained by different sources. As can be seen, the value obtained for $p_b(T)$ by our analysis is in good agreement with the estimation made by Raman-scattering spectroscopy.

The parameters λ and μ , beside being a measure of the extent of the H-bond network cooperativity, are also connected to the water supercooling and dissociation limits through the expressions $\mu = 1 - p_b(T_i)$ and $\lambda = p_b(T_h)$ which can be obtained by imposing the conditions $f_4(T_i) = 1$ and $f_0(T_h) = 1$ to Eq. (5). In our case, these temperatures turn out to be $T_i = 231$ K and $T_h = 516$ K (see Fig. 3). The temperature T_i falls in between the

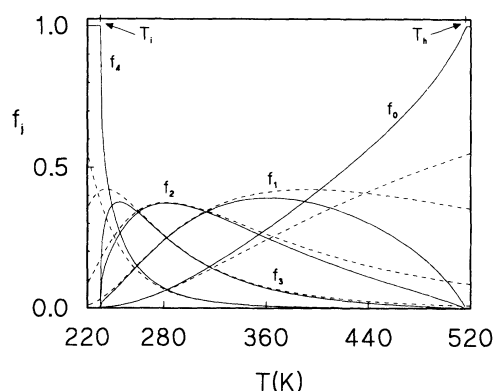


FIG. 3. Fractions of water molecules involved in zero, one, two, three, and four H bonds as a function of temperature, obtained from a random distribution of H bonds (dashed lines) and from the model described in the text in which the H-bond cooperativity is taken into account (solid lines). T_h and T_i are, respectively, the dissociation and crystallization temperatures when cooperative effects are considered (see the text).

TABLE I. Parameters obtained (according to the text) from the best fitting of the density (δ) and thermal expansion coefficient (α) data. Best-fit standard deviations are reported in the last two lines.

v_0	$0.863\ 15\ \text{cm}^3$
v_1	$0.971\ 11\ \text{cm}^3$
v_2	$0.982\ 30\ \text{cm}^3$
v_3	$1.037\ 88\ \text{cm}^3$
α_0	$1.391\ 86 \times 10^{-3}\ \text{K}^{-1}$
β_0	$1.709\ 33 \times 10^{-6}\ \text{K}^{-2}$
α_1	$0.903\ 61 \times 10^{-3}\ \text{K}^{-1}$
α_2	$0.812\ 45 \times 10^{-3}\ \text{K}^{-1}$
α_3	$0.712\ 78 \times 10^{-3}\ \text{K}^{-1}$
E	$153.48\ \text{cal mol}^{-1}$
T_0	$182.4\ \text{K}$
T_c	$1149.1\ \text{K}$
λ	0.2196
μ	0.1404
σ_δ	4.1×10^{-5}
σ_α	3.9×10^{-6}

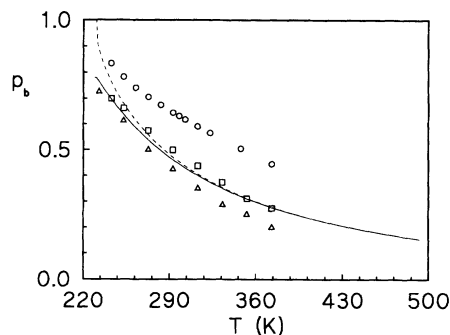


FIG. 4. Probability of forming an H bond as a function of temperature: Open circles, Bertolini *et al.* [25]; open triangle, Hare and Sorensen [8]; open squares, Raman result from D'Arrigo *et al.* [33]; solid lines, p_b [Eq. (8)], and dashed line, p_3 [Eq. (5)] as calculated in the text.

homogeneous nucleation value (232 K) [2] and the power-law-predicted stability limit (228 K) [1,2], whereas the temperature T_h is 72 K below the estimated stability limit of superheating (588 K) [3]. It should be emphasized that T_h represents the limit beyond which no H bonds exist, namely, the state of dissociated liquid, and not the superheating limit which, on the other hand, is determined by the van der Waals interaction and is then expected to occur at higher temperature.

Moreover, it has to be remarked that the temperatures T_0 and T_c , which appear in Eq. (8) and in Table I, would represent the water supercooling and dissociation limits in the hypothesis of a random H-bond network and thus should be lower and higher than T_i and T_h , respectively, i.e., the correlation between the H bond raises the temperature of solidification and lowers the dissociation one.

By comparing Eq. (10), Fig. 2, and Fig. 3, it turns out

$$K_T = \left[\frac{\partial \ln[\delta(T,P)]}{\partial P} \right]_{T,P=1} = \left[\frac{\sum_{j=0}^4 \left[V_j(T,P) \frac{\partial}{\partial P} f_j(T,P) + f_j(T,P) \frac{\partial}{\partial P} V_j(T,P) \right]}{\sum_{j=0}^4 V_j(T,P) f_j(T,P)} \right]_{T,P=1} \quad (12)$$

We should argue that the divergent behavior of the isothermal compressibility could be related to the increase of these derivative values as the temperature is lowered, similar to what happens for the thermal expansion coefficient.

The best fit of the experimental compressibility data [34] by Eq. (12) is shown in Fig. 5. The parameters of the fit are reported in the caption. The agreement is good except for the high-temperature points where the fit curve falls below the experimental data.

The value of the parameters γ_j , which take into account the effect of the patch geometry on the probability

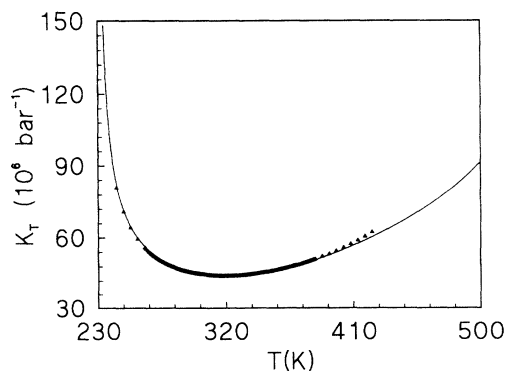


FIG. 5. Water isothermal compressibility as a function of temperature. The solid line represents the best fit of the literature experimental data by Eq. (12) obtained with the following parameter values [see Eqs. (A6) and (A8)]: $\partial_P V_0(1) = 91.08598 \times 10^{-6} \text{ cm}^3 \text{ bar}^{-1}$, $\partial_P V_1(1) = 14.16079 \times 10^{-6} \text{ cm}^3 \text{ bar}^{-1}$, $\partial_P V_2(1) = 0.6225851 \times 10^{-6} \text{ cm}^3 \text{ bar}^{-1}$, $\partial_P V_3(1) = 2.325875 \times 10^{-9} \text{ cm}^3 \text{ bar}^{-1}$, $\gamma_0 = 0.148354$, $\gamma_1 = 0.547805$, $\gamma_2 = 0.055736$, and $\gamma_3 = 0.055736$.

that the anomalous negative value of α below 0°C can be related to the fast increase of the four-bonded water fraction which, on the other hand, is a direct consequence of the cooperative structuration of the H-bond network. In fact, as the temperature is lowered, the fraction of four-H-bonded molecules undergoes a fast increase, reaching its maximum value of 1 at the temperature T_i . The slope of the $f_4(T)$ curve is negative and increases rapidly, upon lowering the temperature, becoming the predominant term in Eq. (10).

A similar behavior could be expected for the isothermal compressibility also. In fact, by replacing temperature with pressure on the right-hand side of Eq. (10), a relationship for the isothermal compressibility is obtained which depends on the derivative of the fractions with respect to the pressure (see the Appendix). Actually, at atmospheric pressure we have

of breaking a LHB under the action of the pressure (see the Appendix), indicates that, by increasing the pressure, it is much easier to break the bonds in the patches with three and two LHB's than in those with one and four bonds. Actually, in the four-bonded patches the molecules are arranged in a regular lattice; thus they behave as a crystalline solid. On the other hand, it is reasonable that in the patches with one H bond, the pressure principally affects the volume changes rather than the bond breaking. This particular behavior is responsible for the shift of the compressibility minimum to higher temperature with respect to the temperature of maximum density: α and K_T depend on the water fractions in a similar way [see Eqs. (10) and (12)]; thus, if there were no difference in the temperature dependence of the pressure and temperature derivatives of the fractions, the maximum density and the minimum compressibility would occur at the same temperature.

FREE-VOLUME-FLUCTUATION CONTRIBUTION TO THE WATER SELF-DIFFUSION

In the previous sections we have analyzed the principal characteristics of the H-bond network and have estimated the distribution of the water fraction as a function of the temperature. In order to evaluate the water self-diffusion coefficient by means of Eq. (1), we still need to calculate the diffusion coefficient relative to each species. In such a connection, we should reiterate that, due to cooperative effects, the water molecules belonging to the same species aggregate in patches; within those, due to the homogeneous composition, the diffusion process is regulated by mechanisms similar to those occurring in normal liquids, the contribution of the H-bond dynamics having already been taken into account in the derivation

of Eq. (1).

Inside each patch, in order to diffuse, a water molecule has to break all its bonds with the surrounding molecules and a sufficient space has to be available into which it can diffuse [18,19,35]. Within patches of unlike species, the water molecules have different diffusional behaviors which depend on the number of H bonds which are engaged and on the local average density. Since the probability of breaking simultaneously more than one H bond is low, the diffusion coefficient for species 2, 3, and 4 should be very small [for species 4, it is approximately that of the ice ($\approx 10^{-11} \text{ cm}^2 \text{ s}^{-1}$)] and thus can be neglected [7,24,25]. In the patches of four- and three-H-bonded molecules, the vibrational-like behavior should be dominant. For the remaining species 0 and 1, taking into account energy and density fluctuations, the self-diffusion coefficient $D_j(T)$ can be expressed by [35]:

$$D_j(T) = \left\{ 8.04c \left[\frac{T}{M} \right]^{1/2} \bar{v}_0^{1/3} \times \exp \left[- \left[\frac{1.69\bar{v}_0}{v_j(T) - \bar{v}_0} + \frac{E_j}{RT} \right] \right] \right\} \times 10^{-5}, \quad (13)$$

where c is a numerical constant of the order of unity; E_j is the activation energy threshold value per molecule for the state j ; \bar{v}_0 is the close-packed volume per mole; $v_j(T)$ is the molar volume of the species j which is connected to the volume $V_j(T)$, appearing in Eqs. (11) and (A7), by $v_j(T) = MV_j(T)$, M being the molar weight. It should be emphasized that all the molecules participate in the diffusion process through the successive breaking of their H bonds, which correspond to the transition between two nonadjacent levels by multiple successive jumps. This effect is taken into account in both the water-fraction-distribution evaluation and the H-bond network dynamics which gives rise to Eq. (1) [24,25].

By introducing Eq. (13) for the 0 and 1 species in Eq. (1), we have fitted a set of NMR self-diffusion coefficient data, which are the collection of published [2,23,36] and experimental data obtained by the static field-gradient spin-echo technique. The best-fit curve, shown in Fig. 6, has been obtained with the following values for the fitting parameters:

$$\bar{v}_0 = 7.6097 \text{ cm}^3 \text{ mol}^{-1},$$

$$E_0 = 156.32 \text{ cal mol}^{-1},$$

$$E_1 = 892.36 \text{ cal mol}^{-1}.$$

The standard deviation of the fit ($\sigma = 0.017$) is comparable with that ($\sigma_{\text{pl}} = 0.018$) obtained by fitting the same set of data by the equation

$$D(T) = D_0 T^{1/2} \left[\frac{T}{T_S} - 1 \right]^\gamma,$$

the best-fit parameters ($D_0 = 0.87$, $T_S = 225$, and $\gamma = 1.66$) being in agreement with those obtained by Prielmeier *et al.* [6]. The value of the close-packed volume \bar{v}_0 is

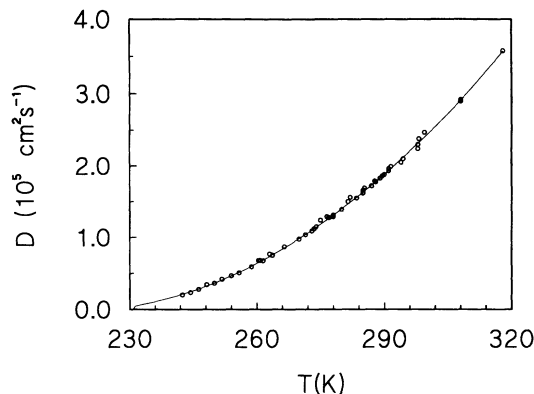


FIG. 6. Experimental ^1H NMR water self-diffusion coefficient data as a function of temperature. The solid line is the best-fit curve obtained according to the text.

consistent with that found in the literature [37]. E_0 represents the non-H-bonded water interaction energy, whereas E_1 represents the average energy necessary to break one H bond.

The value of the energy E_1 is lower than the ligand energy of the H bond (about $5 \times 10^3 \text{ cal mol}^{-1}$). This discrepancy should not be surprising since the activation mechanism in liquid water is not a simple process. In fact, it has been postulated that some strained bonds, the bifurcated H bonds (BHB), should play an important role in effectively reducing the water interaction potential barriers [38,39]. The BHB's are transition-state configurations corresponding to local energy minima with intermediate strength between broken and formed linear H bonds [38,40]. These transition states seem to provide an efficient mechanism of activation and reorganization of the H-bond network, offering a path connecting different LHB configurations through activation barriers lower than the energy needed to break a LHB. We can therefore speculate about the possibility that the low value found for the energy E_1 is due to the effective lowering of the energy barrier accomplished by the BHB's. In addition, since the LHB \leftrightarrow BHB transition is a cooperative process [40], the presence of BHB's in water should introduce a supplementary source of cooperativity in the H-bond network.

As the temperature is lowered, the concentration of the mobile water molecules decreases and the diffusion coefficient in the patches with four-bonded molecules becomes the predominant term in Eq. (1). Therefore, the diffusion coefficient of liquid water can be extrapolated to that of the ice at the temperature T_i of 231 K (see Fig. 3). It should be emphasized that as the self-diffusion coefficient approaches that of ice and then the diffusion length becomes comparable with the molecular dimensions, the non-Markovian character of the diffusion process becomes important and Eq. (1) can no longer be used [24,25,41].

DISCUSSION AND CONCLUSIONS

In the present paper we have presented a model for liquid water which, taking into account both the H-bond cooperativity and the free-volume fluctuations, is able to

reproduce, to a good accuracy, some of the water properties and in particular to interpret the water self-diffusion behavior with the same accuracy as the power law, which, actually, is the best empirical expression reproducing the non-Arrhenius behavior of D . On the other hand, such a power-law behavior constitutes the grounds for the stability limit conjecture, which, assuming a true singularity at the temperature T_S , predict that no continuity of states between the liquid and solid phases can exist [3,4]. On the contrary, our model does not predict any singularity, but some thermodynamic properties such as α and K_T are expected to present a maximum or minimum in the supercooled region. In fact, the only possibility to have a divergence in α and K_T could arise from a divergent behavior of the derivatives $\partial_T f_j$ and $\partial_P f_j$, respectively [see Eqs. (10) and (12) and Appendix A for the symbols]. However, such a possibility should be ruled out on the basis of the normalization condition $\sum_{j=0}^4 \partial_k f_j(T, P) = 0$. In fact, in both Eqs. (10) and (12) the derivatives $\partial_k f_j$ appear in the term $\sum_{j=0}^4 V_j \partial_k f_j$, which, due to the positive and finite value of V_j and to the normalization condition, remains always finite. Moreover, if a continuity of states between supercooled liquid and ice exists, then both α and K_T have to change their trend somewhere in the deep supercooled region. Unfortunately, we are not able to make quantitative extrapolations of our calculations to very low temperature, since for $T = T_i$ two different solutions of Eq. (7) are found. The reason for such a limitation could reside in the simplified description of the cooperative phenomena considered in our model; in Eq. (5) we use a perturbative approach on the random network which proves inadequate when cooperative effects become very important. However, some qualitative indications of a change in the α and K_T trend with temperature can be traced back by the present model.

Statistical-mechanics considerations [7,42] permit the relation of α and K_T to the entropy and density fluctuations in the sample; thus an increase of these quantities should be indicative of the increment of the fluctuation intensity and vice versa. In liquid water the presence of patches with different density and entropy (the four-H-bonded patches being the more ordered and the less dense) induces a very high degree of inhomogeneity and enhances, then, both the density and the entropy fluctuations [7]. If the relative concentration of these patches is changed, the intensity of the thermodynamic fluctuations changes too. In particular, by lowering the temperature, the low-density-high-ordered tetracoordinated patches increase in number and size with a consequent enhancement of the density and entropy fluctuations [7]. However, when the amount of four-H-bonded molecules becomes large with respect to that of the other species, a further increment should result in a higher homogeneity of the sample and then the fluctuations decrease, reaching that of the ice at $T = T_i$. At the point of maximum inhomogeneity, the intensity of the fluctuations should be very large but for a sample of finite size can never diverge [42]. As a consequence of this behavior, both α and K_T should present a change of trend in the deep supercooled region; the scenario should then be that of a damped λ

transition in the proximity of T_i . It should be noted that such a behavior is not incompatible with the Speedy's water equation of state, but is in contrast with its interpretation. In fact, the power-law behavior of several thermodynamic and transport properties, on which the Speedy's argument is based, is the result of the expansion of the pressure P , along an isotherm, as a Taylor series in $\delta - \delta_S$ about the limit of stability defined by $K_T = \infty$. However, such a type of expansion may still work as an approximation if K_T has a maximum whose value is large enough, i.e., in the case of a damped λ transition [3]. In such a case, no divergences would occur and a continuity of states between liquid and solid phases should exist. We should then suggest that the anomalous behavior of liquid water has its origin in the particular structure of the H-bond network and in the overwhelming tendency to a tetracoordination of the water molecules in the supercooled region, rather than in the existence of a singularity or of a critical point, as recently suggest [21]. As the temperature is lowered, patches of four-H-bonded molecules become the emerging structures in the liquid, which is progressively driven toward crystallization at the temperature T_i . However, until crystallization is obtained, the sample still presents configurational disorder, which should prevent the Kauzmann paradox [43]. Moreover, by lowering the temperature, the lifetime of the tetracoordinated patches increases and the probability of finding an icelike cluster of water molecules, which persist for a sufficient time to serve as a seed for the nucleation phenomena, should approach unity by approaching the limit temperature T_i . This effect, which is responsible for the metastability of the supercooled state, could also be considered to explain the correlation between the homonucleation limit temperature and the power-law-determined T_S temperature [2-6].

It should be emphasized that the continuity of states between the liquid and solid phases as described in the present model is a speculative concept since it refers, due to the homonucleation phenomena, to experimentally inaccessible thermodynamic states. In addition, the continuity of states has to be intended only in the liquid-to-solid direction since, due to the metastable character of the supercooled state, once the transition to ice is accomplished, the sample has to be heated to 0°C before the liquid phase can be restored.

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APPENDIX A: TEMPERATURE AND PRESSURE DERIVATIVES OF THE WATER FRACTIONS

In a simplified notation we should indicate the partial derivatives $\partial/\partial T$ and $\partial/\partial P$ by ∂_k , with $k = T$ and $k = P$, respectively.

The temperature and pressure derivatives of the water fractions can be simultaneously calculated from Eq. (4):

$$\partial_k f_{j+1}(T, P) = c_j \left\{ \frac{\partial_k p_j}{q_j^2} f_j(T, P) + \frac{p_j}{q_j} \partial_k f_j(T, P) \right\},$$

$$j=0, 1, 2, 3 \quad (\text{A1})$$

where

$$q_j = 1 - p_j,$$

$$c_j = \frac{4-j}{j+1}$$

and $\partial_k p_j$ are calculated from Eq. (5):

$$\begin{aligned} \partial_k p_0 &= \partial_k p_{b_0} - \lambda \partial_k f_0 - f_0 \partial_k \lambda, \\ \partial_k p_1 &= \partial_k p_{b_1}, \\ \partial_k p_2 &= \partial_k p_{b_2}, \\ \partial_k p_3 &= \partial_k p_{b_3} + \mu \partial_k f_4 + f_4 \partial_k \mu. \end{aligned} \quad (\text{A2})$$

At variance with the temperature dependence, which is simply described by the activation mechanism [$p_b(T)$], the pressure behavior of the water fraction distribution arises from both the pressure-induced modulation of the energy levels [$p_{bj}(P, T)$] and from the perturbation of the H-bond network cooperativity, due to the network geometry changes that are a result of the strains applied to the water molecules (the cooperativity parameters λ and μ are functions of the pressure). Actually, in the present work we are mainly interested in the value of the derivatives $\partial_k p_j$ at atmospheric pressure. On the other hand, it is reasonable to assume that, at least near $P=1$, the cooperative effects are not much affected by the application of a small pressure, i.e., λ and μ are slowly varying

functions of the pressure

$$[\partial_P \lambda(P)]_{P=1} = [\partial_P \mu(P)]_{P=1} \approx 0.$$

Therefore, the terms $\partial_k \mu$ and $\partial_k \lambda$ in Eq. (A2) can be neglected and Eq. (A1) can be written as follows:

$$\partial_k f_{j+1}(T, P) = W_j + Z_j \partial_k f_j(T, P), \quad j=0, 1, 2, 3 \quad (\text{A3})$$

where

$$W_j = c_j f_j(T, P) \frac{\partial_k p_{bj}}{q_j^2}, \quad j=0, 1, 2$$

$$W_3 = \frac{c_3 f_3(T, P) \frac{\partial_k p_{b3}}{q_3^2}}{1 - c_3 f_3(T, P) \frac{\mu}{q_3^2}},$$

$$Z_0 = c_0 \left[\frac{p_0}{q_0} - \frac{\lambda}{q_0^2} f_0(T, P) \right]$$

$$Z_j = c_j \left[\frac{p_j}{q_j} \right], \quad j=1, 2$$

$$Z_3 = \frac{c_3 \left[\frac{p_3}{q_3} \right]}{1 - c_3 \left[\frac{\mu}{q_3^2} f_3(T, P) \right]},$$

$$Z_4 = \frac{\mu}{q_3^2} f_3(T, P).$$

By imposing the normalization condition, which is now $\sum_{j=0}^4 \partial_k f_j(T, P) = 0$, we have

$$\partial_k f_0(T, P) = - \frac{\left\{ \sum_{j=0}^3 W_j + \sum_{j=0}^2 Z_{j+1} W_j + \sum_{j=0}^1 Z_{j+2} Z_{j+1} W_j + Z_3 Z_2 Z_1 W_0 \right\}}{\{1 + Z_0 + Z_0 Z_1 + Z_0 Z_1 Z_2 + Z_0 Z_1 Z_2 Z_3\}}. \quad (\text{A4})$$

The temperature and pressure derivatives of the water fractions can be then obtained by combining Eqs. (A3) and (A4) and by introducing the appropriate term $\partial_k p_{bj}(T, P)$. The term $\partial_T p_{bj}(T, P)$ is easily obtained, at the atmospheric pressure, from Eq. (8), whereas the pressure derivatives $\partial_P p_{bj}(T, P)$ require explicit knowledge of $p_{bj}(T, P)$.

The functions $p_{bj}(P, T)$ take into account the energy changes of the j th state as induced by the pressure. It should then be expected that these functions depend on the product $P V_j(T)$ but also on the geometry of the patch, i.e., on the way in which the H bonds are organized. In particular, the probability of breaking an H bond under the action of the pressure is expected to be higher in the cluster with low connectivity than in the patches with four formed H bonds which are arranged to form a regular lattice. We should then assume that

$$p_{bj}(P, T) = p_b(T) \exp \left[- \frac{(P-1) V_j(T, P) (T_c - T) \gamma_j}{R (T_c - T_0) (T - T_0)} \right],$$

$$j=0, 1, 2, 3 \quad (\text{A5})$$

where γ_j takes into account the patch geometry and $p_b(T)$ is given by Eq. (8). The pressure derivative of p_{bj} is then easily worked out:

$$[\partial_P p_{bj}(P, T)]_{P=1} = -p_b(T) \frac{V_j(T, 1) (T_c - T) \gamma_j}{R (T_c - T_0) (T - T_0)},$$

$$j=0, 1, 2, 3. \quad (\text{A6})$$

APPENDIX B: PRESSURE DEPENDENCE OF THE WATER FRACTION VOLUMES

Concerning the water fraction volumes, we have assumed in Eq. (11) a particular temperature dependence.

The natural way to introduce the pressure in such an equation is the following:

$$V_0(T, P) = V_0(P)[1 + \alpha_0(P)(T - 273) + \beta_0(P)(T - 273)^2],$$

$$V_j(T, P) = V_j(P)[1 + \alpha_j(P)(T - 273)], \quad j = 1, 2, 3 \quad (\text{A7})$$

$$V_4(T, P) = 1/\delta_{\text{ice}}(T, P),$$

which reduce to Eq. (11) for $P = 1$.

Assuming that the expansion coefficients α_j and β_0 are slowly varying functions of the pressure, we set $\partial_P \alpha_j(P) = 0$, $\partial_P \beta_0(P) = 0$, and we then have

$$[\partial_P V_0(T, P)]_{P=1} = \{[\partial_P V_0(P)][1 + \alpha_0(P)(T - 273) + \beta_0(P)(T - 273)^2]\}_{P=1}$$

$$[\partial_P V_j(T, P)]_{P=1} = [(\partial_P V_j(P))[1 + \alpha_j(P)(T - 273)]_{P=1} \quad j = 1, 2, 3. \quad (\text{A8})$$

Moreover, due to the solidlike character of the patches with four H bonds, the pressure derivative of V_4 should be expected to be very small. The additional consideration that at low temperature, where the fraction of four bonded molecules become predominant, the leading term in the isothermal compressibility expression [Eq. (12)] is that depending on $(\partial_P f_4)$ led us to neglect the compressibility of the four bonded molecules and put $[\partial_P V_4(T, P)]_{P=1} = 0$.

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