

Cooperativity and hydrogen bond network lifetime in liquid water

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The lifetime of the H bond network has been calculated as a function of temperature by a statistical five-species model for water in which the H bond cooperativity has been explicitly taken into account. While, on one hand, the Arrhenius behavior of the depolarized Rayleigh scattering data existing in an intermediate temperature region is well reproduced, the model predicts that the H bond lifetime diverges as the supercooled temperature limit is approached. The observed cooperative stabilization of the H bonds in tetracoordinated molecules occurring in the deep supercooled region, where this species becomes the most long-lived one, points out the tendency of the system to unavoidably approach ice rather than to reach a region of dynamical instability.

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The anomalous behavior of liquid water is strictly related to the existence of an extensive network of hydrogen bonds [1,2] which is continuously subject to spontaneous restructuring on a very short time scale [3–7]. The dynamical character of the network is crucial to ensure spatial homogeneity and fluidity typical of the liquid phase and to determine several of the physical properties of water. Therefore, the knowledge of the timing of bond formation and dissolution deserves a great interest for the comprehension of the water behavior.

Average H bond lifetime data, obtained experimentally by depolarized Rayleigh scattering [3–5], are in the picosecond time-scale and display an uncommon Arrhenius behavior, while some of the water properties present strong non-Arrhenius temperature trends whose origin is still being debated [2,8–11]. Conversely, the average bond lifetime obtained by computer simulations [6] shows a power-law behavior but differs from experimental data values by an order of magnitude. Moreover, from computer simulations it emerges that the H bond lifetime depends upon the number of H bonds in which the molecule is engaged [7,12]. This behavior is indicative of a correlation between bonds belonging to the same molecule, which is one aspect of a more general cooperative behavior that will bring tetracoordinated molecules to become the most populated and long-lived species in the supercooled region [7–9,12].

In a recent work we stressed the role of cooperativity in the temperature-dependent evolution of the water H bond network structure in the framework of a statistical five-species model. By this approach, a highly accurate reproduction of the experimental behavior of some thermodynamical and transport properties of water was achieved [8,9]. The model did not predict any singularity in the water thermodynamic and transport properties but was consistent with the existence of a continuity of states between the liquid and solid phases.

In the present work we will instead focus on the

dynamical aspect of the network by investigating the role of H bond cooperativity on the temperature trend of the H bond lifetimes in each water species. This would allow us to both extract an average H bond lifetime to be compared with experimental results and gain a better insight into the evolution of the physical state of water in the deep supercooled region, where the collection of experimental data is made difficult by nucleation phenomena.

We assume liquid water to be described by a system of five quantumlike energy levels corresponding to the five species identified according to the number of H bonds formed by each molecule [2,13–15]. The evolution of the system is described by an appropriate master equation whose equilibrium solution provides the distribution of the water molecules among the five species. In this framework, H bond cooperativity is introduced perturbatively by assuming that the transition rates between adjacent energy levels depend upon the population of the level from which the transition starts [8,9].

The distribution of the water molecules among the five species depends upon the ratio between the transition rates (k_{ij}) to the upper and lower energy levels and thus can be expressed in terms of the probability of forming an H bond as follows [8,9]:

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

$f_j(T)$ are the fractions of water molecules belonging to the j th species and $p_j(T)$ are the probabilities of forming an H bond in each species. The probabilities $p_j(T)$ contain information about the activation mechanisms, phase transition temperatures, and cooperativity. Actually, they take into account the condensation phenomena, which bring water towards ice and dissociated liquid phases, respectively, at the supercooling ($T_i=231$ K) and superheating ($T_h=516$ K) limit temperatures and for the autocatalytic mechanisms involved in the H bond formation [8,9].

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Transition rates between adjacent energy levels are strictly related to the restructuring dynamics of the H bond network. In fact, they are connected to the lifetime of the H bond and to the average time in which a bond remains broken. In particular, the rate constants that are relative to transitions towards lower levels are proportional to the reciprocal value of the H bond lifetime (τ_{Hb_j}), whereas those relative to transitions towards upper levels are proportional to the reciprocal value of the average time (τ_{f_j}) in which the bond remains broken [14–16]:

$$k_{j+1,j} = (j+1) \frac{1}{\tau_{\text{Hb}_{(j+1)}}},$$

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

$$k_{j,j+1} = (4-j) \frac{1}{\tau_{f_j}},$$

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

the coefficients of proportionality ($j+1$) and $(4-j)$ taking into account the different ways in which a molecule in the j th species can undergo a transition.

It has to be noted that the probability of forming an H bond and the bond lifetime explicitly depend upon the water species as due to cooperativity [8,9]. In fact, if cooperativity is absent, H bonds belonging to different species are equivalent and thus have the same lifetime and probability of being formed [2,14,15,17].

By comparing Eq. (1) with Eqs. (2) and (3), we can connect the lifetimes τ_{Hb_j} and τ_{f_j} and the probabilities $p_j(T)$,

$$\frac{k_{j,(j+1)}}{k_{(j+1),j}} = \frac{(4-j)p_j}{(j+1)(1-p_j)} = \frac{(4-j)}{(j+1)} \frac{\tau_{\text{Hb}_{(j+1)}}}{\tau_{f_j}}, \quad (4)$$

from which we can derive

$$\tau_{\text{Hb}_{(j+1)}} = \frac{\alpha(p_j)}{1-p_j} \text{ and } \tau_{f_j} = \frac{\alpha(p_j)}{p_j}. \quad (5)$$

$\alpha(p_j)$ is a function, to be determined, that contains all the information about the restructuring dynamics of the H bonds.

In order to determine $\alpha(p_j)$ some considerations should be made. By definition, the value of the probabilities p_j is restricted to the range 0–1. However, only p_3 can assume the unity value because when the formation of an H bond is a secure event, then all the water molecules are engaged in four H bonds. Conversely, the value 0 can be reached only by p_0 since in this case all the molecules belong to the zeroth species.

Since a bond formed with a probability of 1 remains formed indefinitely, the lifetime of the tetracoordinated molecules and the average time τ_{f_j} of the remaining species have to satisfy the limits

$$\lim_{p_3 \rightarrow 1} \tau_{\text{Hb}_4} = \infty \text{ and } \lim_{p_3 \rightarrow 1} \tau_{f_j} = 0, \quad j = 0, 1, 2, 3. \quad (6)$$

These limits actually imply the formation of ice at the temperature T_i , where $p_3 = 1$ [8,9]. Moreover, when $p_0 = 0$, the H bonds remain indefinitely broken so that we

have

$$\lim_{p_0 \rightarrow 0} \tau_{f_0} = \infty \text{ and } \lim_{p_0 \rightarrow 0} \tau_{\text{Hb}_j} = 0, \quad j = 1, 2, 3, 4. \quad (7)$$

This condition describes a dissociated water phase in which no H bonds exist.

The limits on the right-hand side of Eqs. (6) and (7) imply, respectively, that $\lim_{p_3 \rightarrow 1} \alpha(p_3) = 0$ and $\lim_{p_0 \rightarrow 0} \alpha(p_0) = 0$ [see Eq. (5)]. Since $\alpha(p_j)$ is expected to be a continuous function and its analytical expression is the same for all the water species, it follows that

$$\alpha(p_j) = 0 \text{ for } p_j = 0, 1. \quad (8)$$

By differentiating the expressions of Eq. (5) with respect to p_j and taking into account that

$$\frac{\partial \tau_{f_j}}{\partial p_j} = - \frac{\partial \tau_{\text{Hb}_{(j+1)}}}{\partial p_j}, \quad (9)$$

i.e., the breaking and forming of an H bond are complementary processes, we obtain that $\partial \alpha(p_j) / \partial p_j = 0$ for $p_j = 0.5$. The function $\alpha(p_j)$ is positive and its value at the interval ends is zero [see Eq. (8)]. Therefore, the above condition implies the presence of a maximum for $\alpha(p_j)$ at $p_j = 0.5$.

Further information about the form of $\alpha(p_j)$ can be deduced from the behavior of its derivatives at the extremes of the existence field. The limits of the $\alpha(p_j)$ derivatives at the ends of the definition interval coincide with the limits of the lifetime derivatives, as can be easily seen by using Eq. (8) in the derivative of Eq. (5),

$$\lim_{p_0 \rightarrow 0} \frac{\partial \alpha(p_j)}{\partial p_j} = \lim_{p_0 \rightarrow 0} \frac{\partial \tau_{\text{Hb}_{(j+1)}}}{\partial p_j}, \quad (10)$$

$$\lim_{p_3 \rightarrow 1} \frac{\partial \alpha(p_j)}{\partial p_j} = \lim_{p_3 \rightarrow 1} \frac{\partial \tau_{f_j}}{\partial p_j}. \quad (11)$$

The lifetime derivatives can, in turn, be obtained by differentiating the last two members of Eq. (4):

$$\begin{aligned} \frac{\partial}{\partial p_j} \left[\frac{\tau_{f_j}}{\tau_{\text{Hb}_{(j+1)}}} \right] &= \frac{\tau_{\text{Hb}_{(j+1)}} \frac{\partial \tau_{f_j}}{\partial p_j} - \tau_{f_j} \frac{\partial \tau_{\text{Hb}_{(j+1)}}}{\partial p_j}}{\tau_{\text{Hb}_{(j+1)}}^2} \\ &= \frac{\partial}{\partial p_j} \left[\frac{1-p_j}{p_j} \right] = - \frac{1}{p_j^2}. \end{aligned} \quad (12)$$

By comparing the second and fourth members of Eq. (12) and by using Eq. (4) we obtain

$$\frac{\partial \tau_{f_j}}{\partial p_j} = \left[\frac{1-p_j}{p_j} \right] \frac{\partial \tau_{\text{Hb}_{(j+1)}}}{\partial p_j} - \frac{\tau_{\text{Hb}_{(j+1)}}}{p_j^2}, \quad (13)$$

which combined with Eq. (9) yields

$$\frac{\partial \tau_{f_j}}{\partial p_j} = - \frac{\tau_{\text{Hb}_{(j+1)}}}{p_j} \text{ and } \frac{\partial \tau_{\text{Hb}_{(j+1)}}}{\partial p_j} = \frac{\tau_{f_j}}{(1-p_j)}. \quad (14)$$

Therefore, taking into account respectively Eqs. (6) and (7), we obtain

$$\lim_{p_3 \rightarrow 1} \frac{\partial \tau_{f_3}}{\partial p_3} = -\infty \text{ and } \lim_{p_0 \rightarrow 0} \frac{\partial \tau_{Hb_1}}{\partial p_1} = \infty. \quad (15)$$

By comparing Eq. (15) with Eqs. (10) and (11), taking into account that the analytical expression for $\alpha(p_j)$ is the same for each water fraction, the limits of $\alpha(p_j)$ at the definition interval extremes are finally obtained:

$$\lim_{p_j \rightarrow 0} \frac{\partial \alpha(p_j)}{\partial p_j} = \infty, \quad \lim_{p_j \rightarrow 1} \frac{\partial \alpha(p_j)}{\partial p_j} = -\infty. \quad (16)$$

The simplest expression for $\alpha(p_j)$ that simultaneously satisfies Eqs. (8) and (16) and that has a maximum at $p_j = 0.5$ is a semiellipse,

$$\alpha(p_j) = 2b \sqrt{p_j(1-p_j)}, \quad (17)$$

where b is a parameter having the dimension of the inverse of time, which may be determined by comparison with suitable experimental data.

By introducing Eq. (17) into Eq. (5) and using the probabilities $p_j(T)$ calculated in previous works [8,9], an expression for τ_{Hb_j} and τ_{f_j} can be worked out as a function of temperature.

We show in Fig. 1 the values of τ_{Hb_j} and τ_{f_j} relative to the five different water species as a function of temperature for an arbitrary value of b . Actually, the parameter b is a scale factor that should determine the absolute value of the bond lifetimes but which does not influence their temperature dependence.

By increasing the temperature, due to thermal motion, the H bond lifetime in all the species decreases and, consequently, the average time in which a bond remains broken increases. However, the temperature trend of the lifetimes relative to the different water species is not the same. Actually, by cooling the system the lifetime of tetracoordinated molecules increases much more rapidly than that of the remaining water species, undergoing a divergence at the supercooling limit temperature T_i . Accordingly, the average time τ_{f_0} , in which an H bond remains broken on an unbounded molecule, increases with the temperature, diverging as the superheating limit

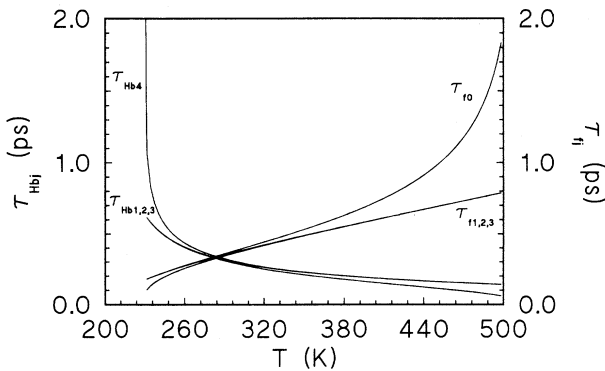


FIG. 1. H bond lifetimes τ_{Hb_j} and average time τ_{f_j} in which an H bond remains broken as a function of temperature for the different water species. The absolute scale of times is relative to a value of $b = 0.167 \times 10^{-12} \text{ s}^{-1}$.

temperature T_h is approached. Therefore, tetracoordinated and unbounded molecules become the most long-lived species, respectively, in the deep supercooled and superheated regions, in agreement with computer simulation results [2,12]. However, it has to be remarked that the lifetime of the tetracoordinated molecules remains well below the value in ice, even at temperatures close to the supercooled limit for less than one degree. This implies that fluidity and spatial homogeneity will be ensured until the phase transition toward ice occurs.

The origin of this particular behavior is the selective self-stabilizing mechanism provided by H bond cooperativity. In fact, if cooperativity is neglected, the H bond lifetime does not depend on the water species and its trend appears similar to that of $\tau_{Hb_{1,2,3}}$ in Fig. 1. The stabilization of the tetracoordinated molecules and the increment of their number in the supercooled region [8,9] could favor the formation of stable long-living icelike water structures that can act as homonucleation seeds, bringing the system towards the ice phase. In other words, by lowering the temperature a cooperativity-induced synergetic deed of concentration increment and time stabilization of tetracoordinated molecules should promote the overwhelming tendency to homonucleation.

In the same way, the stabilization of the unbounded water molecules should favor the onset of a stable phase in which the H bonds are completely broken (dissociated liquid phase). This dynamical picture provides further grounds to rule out the possibility of a spinodal behavior [10] or the existence of a solid-liquid critical point [11] as being the origin of the water anomalies which, on the other hand, should arise from the cooperative growth and dissolution of water aggregates of different species.

In order to compare our species-dependent lifetimes with the experimental average lifetime data, the weighed mean of the lifetimes τ_{Hb_j} over the total number of bonds relative to each species has to be considered:

$$\tau_{Hb}(T) = \sum_{j=0}^3 (j+1) f_{j+1}(T) \tau_{Hb_{(j+1)}}(T), \quad (18)$$

where $(j+1)f_{j+1}(T)$ is the total number of H bonds belonging to the $(j+1)$ th species.

Taking into account Eq. (5) and (17) we have

$$\tau_{Hb}(T) = b \sum_{j=0}^3 \frac{(j+1) f_{j+1}(T) \sqrt{p_j(T)[1-p_j(T)]}}{[1-p_j(T)]}. \quad (19)$$

The fraction $f_j(T)$ of the water molecule in the j th species and the probabilities $p_j(T)$, which contains the information on the cooperativity and activation processes, were previously evaluated [8,9]. Therefore, the only unknown parameter in Eq. (19) is the scale factor b .

The average bond lifetime has been determined by several authors from the analysis of depolarized Rayleigh scattering spectra. The observed frequency spectrum consists of two distinct Lorentzian lines, the linewidth of the broader one being interpreted as the inverse of τ_{Hb} [3-5]. However, the analysis of the experimental spectra provides somewhat different results for τ_{Hb} (with varia-

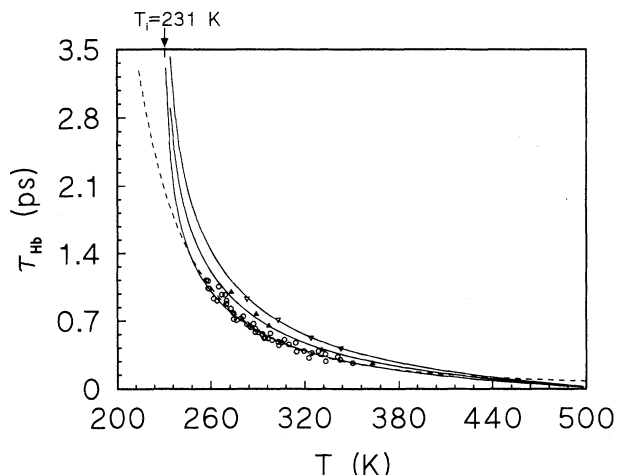


FIG. 2. Average H bond lifetime determined by Rayleigh scattering spectra as a function of temperature. The open circles refer to Conde and Teixeira data [5], closed triangles to data from Montrose *et al.* [3], and open triangles to data from Danninger and Zundel [4]. The solid lines are the best fits with Eq. (19) by using the following values of the parameter b , respectively: $0.167 \times 10^{-12} \text{ s}^{-1}$, $0.201 \times 10^{-12} \text{ s}^{-1}$, $0.238 \times 10^{-12} \text{ s}^{-1}$. The dashed line is the best fit of Conde and Teixeira data with an Arrhenius equation.

tions of around 40%), due to the different deconvolution techniques used. Nevertheless, the temperature dependence of τ_{Hb} was found, in all the experiments, to be virtually the same with an Arrhenius-like behavior [5]. By using Eq. (19) we have fitted the three different experimental data sets existing in the literature [3–5]. As it can

be seen from Fig. 2 our model fits the experimental data to a good accuracy; the different absolute values have been taken into account by varying the scale factor b [see Eq. (19)]. In the same figure we show also the best fit (dashed line) of Conde and Teixeira data obtained by an Arrhenius equation with activation energy and preexponential factor coincident with those reported by these authors [5]. It appears quite evident that in the temperature region in which experimental data exist, our expression for τ_{Hb} is not much different from the Arrhenius expression (see Fig. 2). However, our expression for τ_{Hb} is intrinsically non-Arrhenius, as can be seen when a wider range of temperature is considered. In fact, due to the particular temperature dependence of the probabilities $p_j(T)$ [8,9], which is a consequence of both cooperativity and condensation phenomena, the H bond lifetime that was calculated by our model diverges at the temperature T_i and goes to zero at the superheating limit T_h . Therefore, we might suggest that the temperature behavior of the average lifetime is not due to an intrinsically Arrhenius mechanism, as proposed by some authors [3–6], but rather, might be due to the interplay, in a limited range of temperature, of several different non-Arrhenius phenomena.

In summary, we have introduced cooperativity in an analytical description of the dynamics of water H bond network. We found that, due to cooperativity, in the supercooled region tetracoordinated waters are not only the most abundant, but also the most long-lived ones. We interpreted with a good accuracy the experimental average H bond lifetime data, suggesting that the apparent Arrhenius behavior of the experimental data could be part of a more general temperature trend that unavoidably brings water towards ice and dissociated liquid phases.

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