

HYDROGEN BOND LIFETIME DISTRIBUTIONS IN COMPUTER-SIMULATED WATER

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UDC 532.74

Various hydrogen bond lifetime distribution functions, used to describe the breaking and formation dynamics of these bonds in a computer experiment, are examined and relationships between them are found. The procedures for calculating these functions by the molecular dynamics method are described and the results for water models of 3456 molecules at 310 K are reported. The peak of short-lived spurious H-bonds, which results from short-time violations of hydrogen bonding criteria induced by dynamic intermolecular vibrations of molecules, prevails in the types of distributions most often referred to in the literature. A special distribution that appears to have not been used before is proposed. Along with short-lived bonds, it manifests long-lived ones whose lifetime is determined by the *genuine*, or *random*, hydrogen bond breaking rather than by dynamic. A technique to exclude dynamic effects and reveal the genuine H-bond breaking is proposed. This allows the evaluation of the average lifetime of “true” H-bonds that turns out to exceed 3 ps.

Keywords: computer water simulation, hydrogen bonds, hydrogen bond lifetime.

INTRODUCTION

Hydrogen bonds between molecules in liquid water cannot live long, otherwise it is not clear why water fluidity is little different from that in liquids without hydrogen bonding, for example, in benzene. Indirect information on the lifetime of H-bonds can be derived from experimental data on the relaxation time of various physical properties of water. Thus, the relaxation time for water dipole reorientation at room temperature is about 10 ps [1, 2]. The average hydrogen bond lifetime will roughly agree with this value because reorientation is impossible without breaking at least one H-bond. However, experimental methods cannot yield information on the detailed hydrogen bond dynamics. It can be found only through computer simulation by the molecular dynamics method.

A mere examination by this method of the “life stories” of water molecules shows a high variety in hydrogen bond lifetimes ([3], p. 229), some bonds living a few tens of picoseconds. The quantitative analysis of the breaking and formation dynamics of H-bonds shall describe statistical patterns observed in large ensembles of hydrogen bonds. Stillinger [4] has proposed to use for this analysis the language of correlation functions common in statistical physics. In computer simulation, Rapaport was the first to use this language [5]. Since then over 30 papers [6-34] have been published on the molecular dynamics study of patterns for breaking hydrogen bonds in both water and other systems with hydrogen bonds [12, 14] under different thermodynamic conditions. In addition to correlation functions, various types of distribution functions have been used that are more adequate to the problem. Unfortunately, it is often impossible to understand just what function the

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particular authors used because definitions of the functions and their calculation procedure are not clearly enough described. A. Luzar [19] has tried to find interrelations between different types of the distribution functions, but her analysis is, unfortunately, incomplete and insufficient.

In this work, we make an attempt at completing and extending the results of the analytical part in Luzar's paper. We give precise definitions of various probability distribution functions describing the breaking and formation dynamics of hydrogen bonds and establish their interrelations. Procedures to calculate these functions in a computer experiment are described and their calculation results for one model of water are presented.

1. DEFINITION OF HYDROGEN BONDING

As known, in a computer experiment the full potential of interactions between molecules is set without distinguishing hydrogen bonding in it. Some additional criteria have to be introduced to show between which molecules this bonding occurs. The simplest criterion is geometrical. Let us assume that water molecules form H-bonds if the distance between their oxygen atoms does not exceed some boundary value $R_{OO} < R_{OO}^*$. This criterion can be refined by limiting the distance between oxygen and hydrogen atoms in the neighboring molecules ($R_{OH} < R_{OH}^*$) and the values of different angles in the hydrogen bridge [1, 34, 35]. For example, in our calculations, the results of which are shown below, we have used boundaries $R_{OO}^* = 3.3 \text{ \AA}$ and $R_{OH}^* = 2.45 \text{ \AA}$, but the angles were not restricted. Other, more sophisticated, criteria are also applied [29, 34], but they all introduce a conditional boundary in the particular parameter spaces differentiating between H-bonded and not H-bonded pairs of molecules.

The presence of a fixed boundary in the H-bond criteria arouses an unavoidable difficulty of differentiating between various situations of the existence of hydrogen bonds in the computer experiment. At any position of the boundary in liquid and amorphous water, a large fraction of pairs of molecules has characteristics close to boundary ones for a long enough time. It is impossible to make an unambiguous conclusion whether these pairs of molecules form the H-bond or not. Let us consider the H-bond between some molecules *A* and *B*. Due to intermolecular vibrations (translational and librational) the distance between them (quasi)periodically changes. These vibrations, with a period of about 100 fs, are well seen in Fig. 1 (similar images can be found in [3, 22-24]).

In the process of vibrations, the distance R_{OO} can sometimes "incidentally," for 10-20 fs, go beyond the hydrogen bond criterion (see Fig. 1 near $t = 2$ ps). No change in the form of vibration is observed, and a small enhancement of the R_{OO}^*

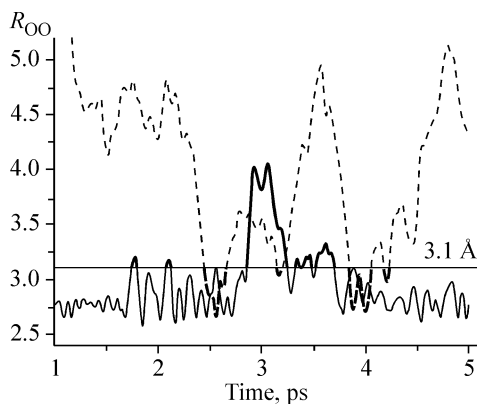


Fig. 1. Typical change in the R_{OO} distance between *B* (solid line) and *C* molecules (dash line) and the molecule *A*. Heavy lines show trajectory portions that "randomly" violated the hydrogen bonding criterion accepted here as $R_{OO} < 3.1 \text{ \AA}$.

boundary can eliminate these disruptions. Therefore, molecules A and B can be assumed to be still H-bonded. However, the computer, according to the geometrical criterion, will indicate the hydrogen bond breaking. This is the first situation that can be called a *spurious breaking* of the H-bond. Short-lived H-bonds may appear between spurious breakings, and we will call them *virtual* hydrogen bonds.

The second situation corresponds to the case when another molecule C , not forming the H-bond with the molecule A , approaches it, due to diffusion motion, at a distance of $R_{OO} < R_{OO}^*$ for a short time (see bold dashes in Fig. 1 near $t = 2.5$ ps and 4 ps). This situation can be called a *spurious formation* of the H-bond (or a *spurious H-bond*). The intervals of the existence of these $A...C$ “bonds” are obviously shorter than the lifetime of virtual bonds in the first situation.

Finally, the third situation is the *genuine breaking* of the hydrogen bond. The H-bond between the molecule A and a certain molecule B experiences *genuine* breaking if molecules A and B quickly move apart from each other for a time noticeably exceeding that of a single oscillation (although later they can join again). The $A...B$ H-bond switches, as a rule, to the $A...D$ H-bond with some other molecule D . Fig. 1 demonstrates the genuine (here temporary) breaking of the H-bond near $t = 3$ ps (molecule D is not shown). A good example of H-bond switching can be seen in Fig. 4 in [22].

The two first situations (spurious breaking and spurious bond) relate to the behavior of a fixed pair of H-bonded molecules. It is *dynamic*, though irregular, because the motion of this pair of $A...B$ molecules is disturbed by thermal fluctuations of the environment. On the contrary, the genuine bond breaking, i.e., the $A...B$ bond switching to the $A...D$ bond at a certain moment, is *random* in the sense that the moment of switching is not only controlled by the $A...B$ bond dynamics, but it is the result of complicated collective motions of the whole system. In the first approximation, the switching of bonds can be considered to be instantaneous, jump-like, which is commonly assumed in theoretical models of water dynamics [40, 41], but the detailed molecular dynamics indicates “slow jumps” [1].

When the hydrogen bond breaking is mentioned, the *genuine breaking* is meant. In the computer experiment, though, the genuine breaking is inevitably confused with spurious breaking and spurious bonds because of the used conditional criteria for the H-bond. It is desirable to avoid them somehow. Many authors have tried to do this, but the problem cannot be considered to be solved. It is typical of many authors to state that they do not emphasize that MD calculations can only provide approximate values of H-bond lifetimes [16] or that it is not easy to unambiguously define the mean H-bond lifetime τ_{HB} because of fast librational motions that rearrange the H-bond network producing the breaking and subsequent reformation of H-bonds in short time intervals [31]. We believe that to solve this problem, first of all, it is needed to find out how the spurious breaking and spurious bonds manifest themselves in different distribution functions of hydrogen bond lifetimes.

2. DIFFERENT TYPES OF DISTRIBUTION OF HYDROGEN BOND LIFETIMES

The autocorrelation function $C(t)$ is most often calculated. It is the probability that the H-bond existing at the instant $t = 0$ will also exist at the next instant t , regardless whether the bond was broken or not in the interval $[0-t]$ and whether it will exist after the instant t [5, 8, 9, 16-19, 21, 25-34]. Of course, such a function describes the weakening over time of some correlations in the H-bond dynamics, or, as they say, characterizes the structural relaxation of H-bonds. However, it is not directly related to the hydrogen bond lifetime. This correlator turns out to be useful for other tasks such as a comparison of the rate of decrease of correlations in bulk water with that at the interface [30], in solvate shells [25, 26, 32], or at different interaction potentials [28].

If the correlator $C(t)$ is calculated only up to the moment of the first H-bond breaking, then we obtain the H-bond survival probability in the time interval $[0-t]$. We will denote this function by $C_a(t)$, while the probability of the first H-bond breaking in time t after we have detected it at the moment $t = 0$ will be denoted by $P_a(t)$ (index “a” means *after*). Obvious relations link these functions

$$C_a(t) = \int_t^{\infty} P_a(\tau) d\tau, \quad (1)$$

$$P_a(t) = -dC_a(t)/dt. \quad (2)$$

The probability distribution function $P_a(t)$ is assumed to be normalized to unity.

The probability distribution function of the total hydrogen bond lifetime $P_t(t)$ is most significant to our problem. It determines the probability that the H-bond detected at a certain instant of time existed for time t from the moment of its appearance up to the moment of the first breaking (index “t” means *total*). It is very important to realize that there are two variants to determine this distribution that are not differentiated in the literature. Let us start our discussion with the relationship between distributions $P_a(t)$ and $P_t(t)$. We consider an instantaneous configuration of our system, i.e., the state of all its hydrogen bonds at a moment $t = 0$. Then we distinguish bonds in them whose total lifetime amounts to a certain value τ . The probability to detect such a bond over a short time interval $d\tau$ is $d\tau/\tau$, and the probability for the bond to have the lifetime τ is $P_t(\tau)$. The value of the function $P_a(t)$ at the moment t after the initial time is formed by only those bonds whose total lifetime τ exceeds the given time t because all other bonds have already been broken. Therefore

$$P_a(t) = \int_t^\infty P_t(\tau) \frac{d\tau}{\tau}.$$

In this reasoning, the distribution $P_t(t)$ means a fraction of H-bonds that have the total lifetime t in the instantaneous configuration considered, and hence, in any other statistically representative configuration. Therefore, hereafter we denote this distribution by $P_{ic}(t)$, namely the probability of the total H-bond lifetime *in a configuration*. So we write

$$P_a(t) = \int_t^\infty P_{ic}(\tau) \frac{d\tau}{\tau}. \quad (3)$$

It implies

$$P_{ic}(t) = -t (dP_a/dt) \quad (4)$$

None of the authors of [5-34, 42] seem to represent the distribution of H-bond lifetimes as the distribution $P_{ic}(t)$. Another function is usually taken as the distribution of these times (see [6, 7, 19]). Instead of a set of H-bonds in the instantaneous configuration, let us consider the process of formation and breaking of bonds for a pair of molecules in the model at a certain trajectory over a rather long time. The fraction of *time* taken by bonds of the given duration t normalized to the sum of times of all bonds is, due to the ergodic theorem, our distribution $P_{ic}(t)$, i.e., the fraction of bonds with the given total lifetime in any instantaneous configuration. It is possible, however, to calculate the *number* of H-bonds of this duration t on this trajectory. Then we obtain the distribution $P_{tt}(t)$ that can be called the probability of the total H-bond lifetime *along the trajectory*. In other words, in the distribution $P_{tt}(t)$ we calculate the number of pairs of molecules that had a continuous H-bond during time t , whereas in the distribution $P_{ic}(t)$ the total time taken by such pairs is found. Therefore, $P_{ic}(t) = B t P_{tt}(t)$.

The factor B is determined by the normalization condition $1 = \int_0^\infty P_{ic}(t) dt = B \int_0^\infty t P_{tt}(t) dt = B \langle \tau_{tt} \rangle$, i.e., $B = 1/\langle \tau_{tt} \rangle$. So,

$$P_{tt}(t) = \langle \tau_{tt} \rangle P_{ic}(t)/t, \quad (5)$$

where

$$\langle \tau_{tt} \rangle = \int_0^\infty t P_{tt}(t) dt. \quad (6)$$

The value $\langle \tau_{tt} \rangle$ is, by the meaning of the distribution $P_{tt}(t)$, the average hydrogen bond lifetime $\langle \tau_{HB} \rangle = \langle \tau_{tt} \rangle$.

It is also possible to introduce other average time characteristics

$$\langle \tau_a \rangle = \int_0^\infty t P_a(t) dt, \quad (7)$$

$$\langle \tau_{ic} \rangle = \int_0^\infty t P_{ic}(t) dt. \quad (8)$$

Substituting in (8) formula (4) and integrating by parts, we obtain the general relationship

$$\langle \tau_{tc} \rangle = 2\langle \tau_a \rangle. \quad (9)$$

The average $\langle t_a \rangle$ is not expressed through the average H-bond lifetime $\langle t_{HB} \rangle$. However, from (3) and (5) an interesting relationship follows

$$P_a(0) = 1/\langle t_{HB} \rangle. \quad (10)$$

From (7) and (1), by changing the order of integration, it is also possible to obtain

$$\int_0^{\infty} C_a(t) dt = \langle \tau_a \rangle. \quad (11)$$

From (4) $P_{tc}(0) = 0$ follows, which is as it should be according to the meaning of the function $P_{tc}(t)$. As to the value of the function $P_{tt}(t)$ at $t = 0$, it is not expressed through average times. However, it is possible to show that is true.

$$\frac{1}{\langle \tau_{HB} \rangle} P_{tt}(0) = \frac{P_{tc}(t)}{t} \Big|_{t=0} = \frac{dP_{tc}}{dt} \Big|_{t=0} = -\frac{dP_a}{dt} \Big|_{t=0}. \quad (12)$$

A more exotic representation of the distribution $P_{tt}(t)$ is used in the works [23, 24]. It is the so-called rank distribution. If the entire set of lifetime values $\{t\}$ computer calculated for the given model are arranged in increasing order, the rank distribution is the dependence of the lifetime t on its number N in the series: $t = R(N)$. Let the maximum number in the series be N_m and $W = N/N_m$. Then $W(t)$ is what in probability theory is called the probability distribution function of the random variable t [36]. It is calculated by the distribution probability t , i.e., by $P_{tt}(t)$:

$$W(t) = P(\xi \leq t) = \int_0^t P_{tt}(x) dx. \quad (13)$$

Hence, the rank distribution of hydrogen bond lifetimes is

$$t = R(N) = W^{-1}(N/N_m). \quad (14)$$

Other distribution functions such as the reactive flux correlation functions introduced in [17-19] and used by some other authors [20, 28, 30, 33] are set aside here. They are intended to interpret the H-bond breaking dynamics in terms of transition state theory, and their consideration lies beyond the purposes of this study.

3. FREE PATH TIME DISTRIBUTION IN GASES

The problem of the distribution of hydrogen bond lifetimes is similar to that of the free path time distribution in the gas phase. In all treatises and handbooks on gas-kinetic theory the distribution $P_a(t)$ is always discussed, while the distribution $P_{tc}(t)$ is only mentioned sometimes. Nowhere could we find either the formula for $P_{tc}(t)$ or relationships (3), (4) linking these two types of distributions. Everywhere it is stated that

$$P_a(t) = (1/\tau_0) \exp(-t/\tau_0), \quad (15)$$

where τ_0 is the average free path time. By our formulae (3) and (5) it follows that

$$P_{tc}(t) = (t/\tau_0^2) \exp(-t/\tau_0). \quad (16)$$

$$P_{tt}(t) = (1/\tau_0) \exp(-t/\tau_0). \quad (17)$$

Of course, $\langle t_{HB} \rangle = \tau_0$ (see (6)). The function $P_{tc}(t)$ at $t = 0$ is zero and has a maximum at $t_m = t_0$ (Fig. 2).

Instantaneous collisions of molecules in gas can serve a good model for the *genuine* breaking of hydrogen bonds. Then the free path time corresponds to the total time of the hydrogen bond existence, and instantaneous collisions are responsible for the H-bond breaking for infinitely small time. The fraction of these infinitely small parts along the trajectory is $P_{tt}(0)$ in terms of distribution functions that we introduced. But at the same time, it is simply the frequency of collisions $1/\tau_0$. Therefore, $P_{tt}(0) = 1/\tau_0$, in full compliance with (17). The difference of $P_{tt}(0)$ from zero in water shows the occurrence of *genuine* hydrogen bond breaking not caused by a violation of the artificial H-bond criteria, and $P_{tt}(0)$ provides evaluation of

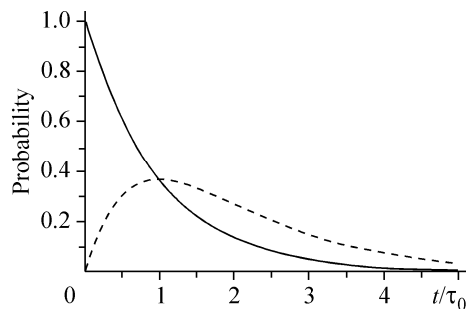


Fig. 2. Distribution functions of free path times in gases. Solid line shows $\tau_0 P_a(t) = \tau_0 P_{it}(t)$, dashes depict $\tau_0 P_{ic}(t)$.

the breaking. Luzar [19] believes that $P_{it}(0) = 0$ because most bonds are formed through libration-like motion that makes an immediate breaking unlikely. This reasoning, though, ignores the occurrence of the *genuine* (“random,” “instantaneous”) breaking of H-bonds.

The time τ_0 in our terminology is $\langle \tau_a \rangle$. Then, according to (9), $\langle \tau_{ic} \rangle = 2\tau_0$. The relation between these two times is interpreted differently in the gas-kinetic literature. In the classic treatise [37], Boltzmann repeats Clausius’s (who first derived formula (15)) arguments by which he wanted to prove that $\langle \tau_{ic} \rangle = \langle \tau_a \rangle$. However, this verbal argumentation is unconvincing. The majority of authors ignore this problem and only in the Shtrauf’s textbook [38] we could find the correct relationship $\langle \tau_{ic} \rangle = 2\tau_0$, but it had also been obtained through verbal reasoning.

4. DISTRIBUTION OF NON-LIFETIMES OF HYDROGEN BONDS

The dynamics of hydrogen bonds substantially differs from the dynamics of molecular motion in the gas phase. In the gas phase, the molecular free path after a collision instantly alternates with another free path. However, if the proton of a water molecule A has ceased to participate in hydrogen bonding with molecule B (we denote it as H-bond breaking), then some time later it can again take part in H-bonding with it. We call the time interval between successive formations of the $A\dots B$ bond the “non-lifetime” of the hydrogen bond, and the distribution of non-lifetimes is denoted by $P_{nl}(t)$.

5. COMPUTER CALCULATION OF DISTRIBUTION FUNCTIONS

We have already mentioned that it is often impossible to understand what kind of distribution function the authors of the works [5-34] calculated. In order to avoid these ambiguities, we describe the calculation procedures for the distributions used in detail.

The result of molecular dynamic simulation is that we have a sequence of atomic configurations corresponding to the system states in discrete moments of time separated by a step of simulation Δt_{MD} . Using one of the hydrogen bond criteria, we can calculate the hydrogen bond network for each of these configurations, i.e., a table showing with which molecules each molecule of the system forms the H-bond.

Let us consider the bonds that existed at the time $t = 0$ and follow the configurations after the given one, fixing the moment of the first breaking of each bond considered $t_{after} = t_a$. The distribution of the values obtained (normalized to their number at the moment $t = 0$) is just the distribution $P_a(t)$. Similarly, it is possible to trace the bond from the initial moment to the moment of its appearance $t_{before} = t_b$ and to obtain the distribution $P_{before}(t) = P_b(t)$. For each bond, its personal t_a and t_b are not necessarily the same. A summation of times t_a and t_b of each bond yields the total hydrogen bond lifetime $t_{total} = t_t$. It is clear that well averaged distributions of these times do not differ from each other, i.e., $P_a(t) = P_b(t)$, and the sum of their averages shall equal the average total lifetime $\langle \tau_t \rangle = \langle \tau_a \rangle + \langle \tau_b \rangle = 2\langle \tau_a \rangle$, which is well consistent with (9).

Although the distributions of times t_a and t_b are equivalent, the distribution of their sum t_t in any of the two above considered representations substantially differs from $P_a(t)$. If we consider a particular configuration, find t_a and t_b for each of its bonds, calculate its total lifetime ($t_t = t_a + t_b$), build the distribution of these times, then average it over a sufficient number of configurations (preferably independent), we will finally obtain the total lifetime bond distribution in any instantaneous configuration under given conditions of simulation $P_{ic}(t)$. Here the lifetime of the bond present in several successive configurations will be taken into account proportionally to the number of these configurations, i.e., proportionally to its lifetime. We call this distribution the configuration-averaged distribution.

If we follow the bonds in the simulation process, fixing the moment of their appearance and breaking and allowing for each bond only once at the moment of its breaking (when its lifetime becomes known), regardless to which configuration it belongs, then we will apparently obtain a different kind of distribution. It will be the trajectory-averaged distribution $P_{tt}(t)$.

The second distribution shows the probability for the emerging bond to be broken in time t . The first distribution reveals the fraction of bonds of any instantaneous configuration in the hydrogen bond network whose total lifetime is equal to this time t . Differences in these distributions can be illustrated more vividly by the following example. Let us consider a system containing only two bonds, the first of which is alternately broken and reformed, while the second remains unbroken. On the trajectory distribution of this system, we observe a high peak at the lifetime of the first unstable bond and a very low one at the second lifetime of the stable bond. At the same time, in the configuration-averaged distribution $P_{ic}(t)$, the peak corresponding to the stable bond turns out to be higher than that of the unstable bond to the extent in which the total lifetime of this bond is longer.

The non-lifetime of the hydrogen bond is determined as follows: if at the moment $t = 0$ the bond exists, and at the moment Δt_{MD} (at the next step of comparison) it is absent, and it is detected again only at the moment t , then we assume the bond non-lifetime to be $t - \Delta t_{MD}$. The distribution of these times is normalized to the number of broken bonds at the next step; in this case, the integral from zero to infinity is 1. This distribution of lifetimes $P_{ni}(t)$ is similar to the trajectory-averaged distribution of total lifetimes $P_{tt}(t)$. The broken H-bond can be reformed again between a pair of molecules in a very long time because even in infinite time there is a possibility for former neighbors to occasionally meet.

All distribution functions presented here were calculated by the molecular dynamics method for a water model with a number of particles $N = 3456$ at a temperature of 310 K and a density of 1 g/cm³. We used the Poltev–Malenkov interaction potential [39]. All distributions were averaged over the trajectory of 500 ps to 1-2 ns long. The simulation step Δt_{MD} was 1 fs in most calculation. Data obtained with another step are specially noted.

6. CALCULATION RESULTS AND DISCUSSION

Fig. 3 depicts the distribution $P_a(t)$. Almost all authors have calculated it, and they all noted its non-exponential character with a faster decline at small times. In our case, the distribution reaches the exponential asymptote with a characteristic time of 1480 fs in about 2 ps. A deviation from the exponent at smaller times is usually attributed to the effect of librational motions. However, the form of the distribution $P_a(t)$ is too inexpressive to yield more meaningful information.

The diagrams of the of total H-bond lifetime distribution have a quite different form (Figs. 4 and 5). The trajectory-averaged distribution $P_{tt}(t)$ has a sharp maximum at 13 fs. Functions of this type were calculated in [6, 7, 19]. However, the configuration-averaged distribution $P_{ic}(t)$ is most informative. It does not seem to have been built in any of the articles that we reviewed [5-34, 42]: nothing similar to our representation of $P_{ic}(t)$ can be found there. In the distribution $P_{ic}(t)$, three maxima are observed at 30 fs, 150 fs, and 700 fs. It reaches the asymptote corresponding to the exponent $P_a(t)$ at about 3 ps (Fig. 5b). The contribution of this asymptote, according to (16), has a hump shape with a maximum at $t = 1.48$ ps. An advantage of the function $P_{ic}(t)$ against $P_a(t)$ and $P_{tt}(t)$ is that it allows one to observe in detail what occurs to the left of this maximum.

It is well seen in Fig. 5 that at least three distributions with three different lifetimes are required to fill the gap to the left from the maximum at $t = 1.48$ ps. There is no need to give a special physical meaning to the forms of these distributions

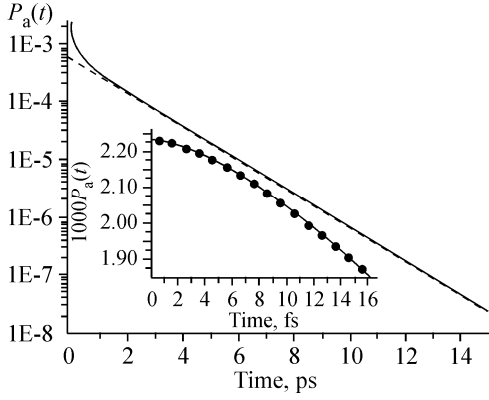


Fig. 3. Distribution $P_a(t)$ is shown by the solid line. Dashes show the asymptote $P_a(t) = 0.000544 \cdot \exp(-t/1480)$. The inset shows a portion at small times approximated by the polynomial $P_a(t) = 0.00223 - 4.25 \cdot 10^{-6}t + \dots$

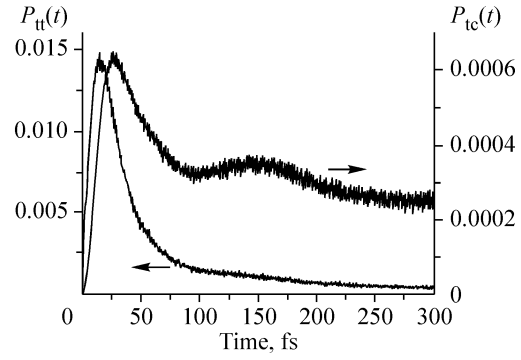


Fig. 4. Comparison of two types of distribution of the total hydrogen bond lifetime. For $P_{tt}(t)$ the Y axis is on the left; for $P_{tc}(t)$ it is on the right. Molecular dynamics with a step of $\Delta t_{MD} = 0.2$ fs; trajectory 2 ns long. The distributions were calculated independently in the computer experiment; they are well recalculated into each other by formula (5).

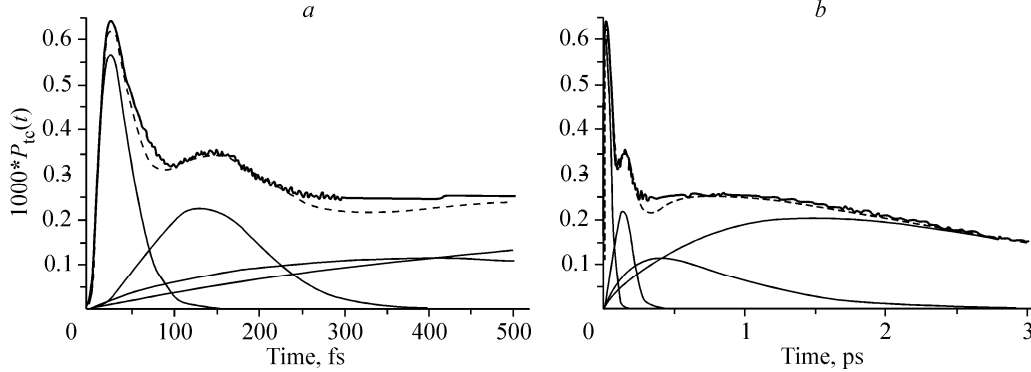


Fig. 5. Total lifetime distribution $P_{tc}(t)$: (a) over 500 fs, (b) over 3 ps. Dashes depict approximation by the function $P_{tc}(t) = 10^{-4} [10.6(t/13)^2 e^{-t/13} + 6(t/133)^2 e^{-(t/133)^2} + 3(t/400) \times e^{-t/400} + 5.44(t/1480) e^{-t/1480}]$; thin lines present individual terms of this function.

that we used for the approximation in Fig. 5. However, something useful can be derived from them. The first two peaks cannot be fitted to the exponent that yields width too large. Therefore we have to multiply it by an additional linear term (see the formula in the legend to Fig. 5). This may indirectly indicate that these peaks do not describe the random breaking of H-bonds, but they are of dynamic origin. We believe that the peak at 13 fs corresponds to spurious bonds, whereas the peak at 133 fs can be assigned to virtual bonds between spurious breakings (definitions are given in Section 1). The third distribution can be represented by the exponent with a time of 400 fs. Exponential distributions must correspond to the genuine breaking of hydrogen bonds. The presence of two exponents in our approximation certainly does not mean that the model contains hydrogen bonds of two types. It indicates only that the breaking probability distribution cannot be described by one lifetime. Still the presence of the exponential asymptote is indisputable. This results in that the $P_a(t)$ derivative is different from zero at $t = 0$ (see the inset in Fig. 3) and, according to formula (12), it leads to that $P_{tt}(0) \neq 0$.

The distributions obtained (before any approximations) are characterized by the following average characteristics:

$$\langle t_{HB} \rangle \equiv \langle t_{tt} \rangle = 450 \text{ fs}; \langle t_a \rangle = 1/2 \langle t_{tc} \rangle = 1240 \text{ fs}. \quad (18)$$

If the exponential decay time of 1480 fs is added, then we have three time characteristics of the H-bond dynamics. What do they mean? So far it is only possible to say that they relate to a summary process of the existence of hydrogen bonds in which

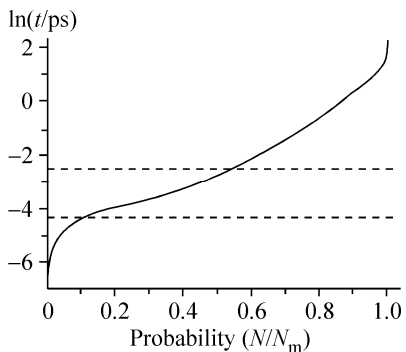


Fig. 6. Rank lifetime distribution. Upper dashes show the position of the kink at 80 fs, according to Tytik [23]. Lower dashes show the position of the distribution maximum $P_{tt}(t)$ at 13 fs (Fig. 4).

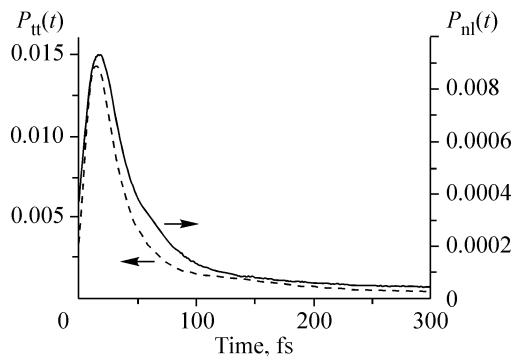


Fig. 7. Non-lifetime distribution $P_{ni}(t)$ is shown by the solid line in comparison with the lifetime distribution $P_{tt}(t)$ that is shown by dashes. Calculated by the trajectory of 1 ns with a step of 1 fs.

both the dynamics and random breaking are intricately mixed. Three different numbers reflect different aspects of this complicated process. Special methods are needed to derive information about the genuine breaking of hydrogen bonds. One of them is considered below (see Section 7).

Fig. 6. shows the rank distribution calculated by formulae (12) and (13) from $P_{tt}(t)$. It resembles a similar distribution for the cluster of 216 water molecules given in the work [23]. We can see that the positions of kinks of this function, being estimated by eye, poorly agree with features of the distribution $P_{tt}(t)$; all the more so, it is difficult to see in it all details distinctly displayed in the distribution $P_{tc}(t)$.

Fig. 7 presents the non-lifetime distribution. The distribution maximum is observed at 17 fs, and the average non-lifetime is about 160 fs. The distribution is normalized to the total number of broken bonds. The 64% of bonds have the non-lifetime less than 0.5 ps. Another 7% correspond to the next 0.5 ps. The value of the integral from zero to 1 ps is 0.71; therefore, 29% of bonds were not reformed during 1 ps. Part of them completely broke. The other part will be reformed later because even in infinite time there is a possibility for former neighbors to meet occasionally. The non-lifetime distribution is very similar to the distribution $P_{tt}(t)$, which has already been mentioned in [19]. We assigned the peak at 13 fs in $P_{tt}(t)$ to spurious bonds that appear when the third molecule approaches the given $A...B$ pair for a short time. The fact that the peak of the non-lifetime distribution is located approximately in the same place is likely to mean that the approaching molecule slightly forces apart the $A...B$ bond, driving it outside the boundary of the H-bond criterion, and thus leading to the situation of spurious breaking. In any case, the similarity of the distributions $P_{ni}(t)$ and $P_{tt}(t)$ can in no way be considered as trivial.

7. EFFECT OF THE TIME INTERVAL BETWEEN SUCCESSIVE CONFIGURATIONS

Up to now, we have implied that all configurations of the molecular dynamics simulation are used to calculate the distributions and to determine the lifetime of H-bonds. However, we can prepare sequences with any time interval Δt between configurations. The enhanced interval between the configurations compared leads to that the short lived spurious and virtual bonds are less taken into account in the distributions because the short-time breaking of H-bonds can fall on those configurations that were missed in the given sequence. Therefore, for each interval of time between configurations we obtain a certain distribution of probabilities, different from others, and certain values for the average lifetime. Many authors of the works cited here [5-34, 42] have repeatedly calculated the distributions with different intervals between the configurations compared; still this procedure was not systematically analyzed.

Fig. 8 shows the total hydrogen bond lifetime distribution $P_{tc}(t)$ for the intervals between the configurations compared of 1 fs, 5 fs, 25 fs, 125 fs, and 500 fs. As seen from the figure, the plots are almost the same for the sequences with

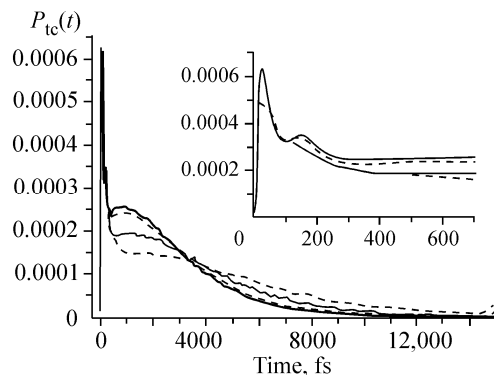


Fig. 8. Distribution $P_{tc}(t)$ calculated with different intervals Δt between compared configuration. From top downwards (by the maximum near 1000 fs): $\Delta t = 5$ fs (does not differ from $\Delta t = 1$ fs), 25 fs, 125 fs, and 500 fs. The inset presents the initial part of the same plots.

a small step between configurations (1 fs and 5 fs). All three maxima, i.e., at about 15 fs, 150 fs, and 700 fs, are drawn very well in both configurations. Only at intervals comparable with these times (25 fs and 125 fs) the distributions begin to noticeably differ from each other. Note that the rest distributions, $P_{tt}(t)$ and $P_a(t)$, differ from each other less, even at a large value of the time interval between configurations.

Fig. 8 shows that an increase in the interval between configurations even up to 500 fs does not completely exclude short-lived (spurious) bonds. The average lifetime slowly increases, but does not tend to saturation (Fig. 10). Therefore, additional procedures are required to derive information on the genuine breaking of H-bonds.

Let us introduce some time limit of the permissible duration of H-bond breaking t_{break} and assume that the temporary bond breaking for a period of no more than t_{break} is not the genuine breaking. When calculating the distributions, we consider this bond to be unbroken and allow for it together with those without any breaking. Fig. 9 depicts the distributions $P_{tc}(t)$ with $t_{\text{break}} = 1$ ps.

As should be expected, the distribution with bond reconstruction after the short-time breaking of less than 1 ps for different intervals between compared configurations is almost the same. Even the distribution with the longest interval of 500 fs differs from the rest only in the first and second points. The same stability is also demonstrated by the average lifetime of bonds with permissible temporary breaking (Fig. 10). It should be noted that the numbers given in the figure are obviously underestimated because a rather high number of bonds has the lifetime longer than 15 fs under this definition (the distribution has not yet declined to zero, see Fig. 9).

The general form of distributions after 3 ps is well described by formula (16) for random breaking in the gas phase with time $\tau_0 = 3.5$ ps (Fig. 9). This time is close to the average H-bond lifetime $\langle \tau_{\text{HB}} \rangle = 1/2 \langle \tau_{tc} \rangle = 3.2$ ps (Fig. 10). Hence, three different times noted in (18) now become almost equal to each other. Therefore one may assume this procedure of levelling the contributions of spurious breakings and spurious bonds to provide better understanding of properties of the genuine hydrogen bond breaking.

CONCLUSIONS

We have examined different hydrogen bond lifetime distribution functions and established relationships between them. In the distribution of total trajectory-averaged lifetimes $P_{tt}(t)$, preferred by many authors, only one peak at ~ 15 fs is distinctly seen. Substantially more details are revealed by the configuration-averaged lifetime distribution $P_{tc}(t)$. The maxima

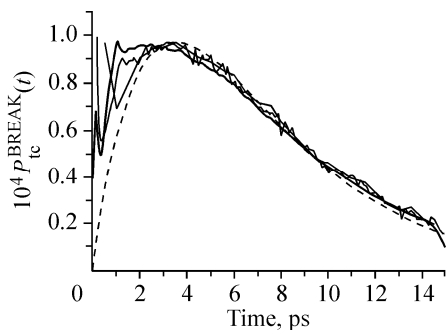


Fig. 9. Distribution $P_{tc}^{\text{break}}(t)$ at permissible temporary breaking of bonds less than 1 ps. Solid lines are the distributions with intervals Δt between compared configurations of 5 fs, 125 fs, and 500 fs. Dashes depict the exponent with time 3.5 ns, i.e., $P_{tc}(t) = 2.64 \cdot 10^{-4} (t/3500)e^{-t/3500}$.

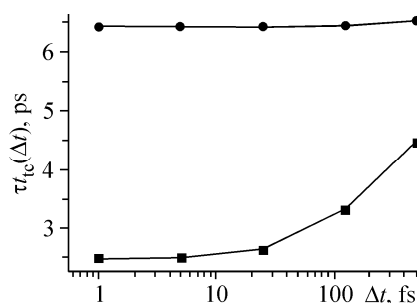


Fig. 10. Dependence of the average hydrogen bond lifetime $\langle t_{tc} \rangle$ on the interval between compared Δt configurations: (at the bottom) without breaking, (on the top) with permissible breaking less than 1 ps.

of this distribution at about 15 fs and 130 fs are spurious H bonds and virtual bonds formed between spurious breaking. They arise due to short-time violations of the hydrogen bond criteria in dynamic intermolecular vibrations of molecules. Thus, these two first maxima reflect the least interesting moments in the dynamics of H bonds.

The *genuine breaking* of hydrogen bonds is of much more interest. It is determined by “random” H-bond switching from one molecule to another rather than by intermolecular vibrations. The third maximum of the distribution $P_{tc}(t)$ at ~ 700 fs and a remote asymptote, well described by the exponent in the distribution $P_a(t)$ and by the corresponding “humpy” function (16) in the distribution $P_{tc}(t)$, correspond to genuine breaking. This asymptote is similar to the free path time distribution in gases, and instantaneous collisions in the gas phase that interrupt a free path are a good model for the random, “instantaneous” breaking of hydrogen bonds. The presence of the exponential asymptote proves the existence of the random H-bond breakings. The latter also determines the non-zero value $P_{tc}(0)$, which, according to (17), is a frequency of the instantaneous breaking.

In order to diminish the effect of dynamic breaking on the lifetime distribution and thereby reveal the *genuine “random” breaking*, we have used a procedure that simply neglects short-time breaking of bonds. It was assumed that the short-time bond breaking of less than 1 ps is not the genuine breaking, and therefore, the time during which the bond is in this state of short breaking is considered to be a part of its total lifetime. When calculating the distributions, such “discontinuous” bonds were taken into account together with those without any breaking. The interval of the selected permissible breaking of 1 ps exceeds by the order of magnitude the period of librations and is several times less than the expected average lifetime of H-bonds between genuine breaking. Hence, it is reasonable to expect the dynamic effects to be suppressed in this procedure, which has been demonstrated by our calculations. However, this method fails to completely eliminate the effect of librations, and further efforts should be made to develop methods to analyze the time evolution of hydrogen bonds.

The work was supported by RFBR grant No. 06-03-32479a.

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