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Resolving the hydrogen bond dynamics conundrum

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This paper analyzes dynamic properties of hydrogen bonds in liquid water. We use molecular dynamics simulation to calculate different probability densities that govern the time evolution of the formation and rupture of hydrogen bonds. We provide analytical connections between these functions. Excellent agreement with our simulation results is observed. We prove transition state theory rate constant to be identical to the inverse of the associated mean first passage time (hydrogen bond lifetime). Hence, the analysis establishes its Arrhenius temperature dependence. We give the explicit relation between reactive flux correlation function for the relaxation dynamics of hydrogen bonds, and their first passage time probability densities. All the different observations in the existing literature, associated with various estimates of hydrogen bonding times in liquid water that are affected (or not affected) by particular bond criteria, as well as by different definitions of hydrogen bond lifetimes applied in simulation, can be easily reconciled within the framework of reactive flux correlation function approach. © *2000 American Institute of Physics.* [S0021-9606(00)51444-5]

I. INTRODUCTION

The elemental dynamic process of rupturing and forming of hydrogen bonds (H bonds) in water is probed indirectly through a number of experimental techniques.[1–5] Computer simulation, on the other hand, provides a more direct quantitative information on the dynamics of H bonds. Over the years, molecular dynamics (MD) studies of the time dependent behavior of H bonds have primarily focused on one property, i.e., the mean hydrogen bond (HB) lifetime, τ_{HB}. In water, librational motions cause an apparent breaking and reforming of an H bond on a very fast time scale.[6] Therefore a broad range of HB lifetimes in water have been reported in computer simulations, depending on how these fast librational motions have been accounted for. In some of the previous works, authors tried to circumvent this problem by adding a temporal definition of an H bond[7–11] to already traditional geometric[12] and/or energetic[13] criteria. The chosen temporal resolution longer than several librational frequencies provided a way of distinguishing *transient* events which are not really bond breaks from ‘‘true’’ breaking of a bond. However, Matsumoto and Gubbins have shown in the case of methanol[14] that molecules which used to have a bond are more likely to reform it than random neighbors are. That means that some memory persists over time longer than the librational period, indicating that a bond can be broken for a significant period of time and still has a greater than random probability of reforming.

In addition to a variety of ways to define an H bond in simulation studies, different HB lifetime definitions may be used. Stillinger was the first to propose several ways to analyze the dynamics of hydrogen bonds in the context of MD.[15] Specifically, one can study correlations in a time series of bonds independent of the history of bond-breaking events. Alternatively, one can consider correlations only for bonds which are continuously intact, and therefore depend on the history of bond breaking. Both lifetime queries can be adopted using the direct counting methods, or alternatively, a correlation function approach. Using the direct counting approach has several drawbacks. For example, calculation of hydrogen bond lifetimes as an average over the duration of individual bonds registered in the simulation[9,10] requires statistics over a period of time much larger than the bond lifetime itself. Thus, HB lifetimes estimated from monitoring individual bonding pairs in the course of the simulation runs can be affected by the length of the simulation and finite size of the system. Rapaport[16] was the first to recognize that in order to estimate meaningful bond lifetimes the quantities that must be extracted from the simulation data are relaxation times obtained from time-dependent autocorrelation functions of population of H bonds which reflect the existence (or nonexistence) of bonds between each of the possible pairs of molecules in the system. Following the proposed analysis of the H bond history by Stillinger,[15] Rapaport[16] calculated two types of autocorrelation functions for MCY water[17] over broad range of temperatures and definitions of an H bond.

1. Autocorrelations for molecular pairs bonded *continuously*, i.e., *without interruptions* over the entire interval from 0 to t (continuous HB correlation function).
2. Autocorrelations for molecular pairs *irrespective of intervening interruptions*, i.e., of possible prior bond breaking and reforming events (intermittent HB correlation function).

A set of relaxation time estimates based on the *assumed* exponential form of the correlation functions have been reported, the continuous lifetimes extracted from case (1) being about one order of magnitude smaller than intermittent lifetimes [obtained from case (2)], and both being dependent

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on the H bond criteria used in the simulation. Note that in case (2) bonds which have been briefly ''interrupted'' by librational motions will continue to contribute to the correlation function at later times. This leads to much longer lifetimes than obtained in case (1). Since this first, yet elaborate attempt to understand H bond dynamics in water almost 20 years ago[16] other authors have typically focused on either of these methods using a particular potential and definition for a bond to estimate HB lifetimes in several systems: ambient water,[18] pure supercritical water,[19–21] solvation in supercritical water,[22] pure methanol,[14] pure ethanol,[23] water near hydrogels,[24] by assuming a ''quasiexponential'' decay of calculated correlations functions.

A more rigorous way to determine the nature of the relaxation of H bonds in H bonded liquids is the approach used by chemical dynamics community to calculate reactive flux HB correlation functions and determine the actual rate constant, i.e., $1/\tau_{\mathrm{HB}}$, from a plateau value, if it exists.[25,26] In our previous work[27] we give a succinct quantitative description of the interplay between diffusion and bond breaking/making that gives rise to a seemingly complicated time correlation function for the hydrogen bonds in water.[27] The physics behind the observed nonexponential time dependence of the calculated correlation functions is given.[27] Using the reactive flux correlation function approach[28–31] and the appropriate phenomenology for the kinetic process under consideration[27] we demonstrate this dynamics to be very simple, being characterized with rate constants for bond breaking and making. In other words, what makes the H bond dynamics apparently complicated is translational diffusion that introduces a continuum of time scales.

The distribution of HB lifetimes introduced by Stanley and his co-workers[32–34] provides a complementary view of HB dynamics. This distribution is determined from trajectory calculations by recording the separate length of time over which a bond (that is created at time zero) is continuously alive. It has been found to have different behaviors: exponential distribution,[35] roughly exponential distribution,[32] power-law distribution,[33] and ''neither power-law nor exponential'' distribution.[34] Finally, the conclusion has been given[34] that the analysis based on the distribution of bond lifetimes cannot present a clear picture of the dynamics due to the sensitivity on all time scales to the choice of bonding definition. Since it has been shown experimentally[1,2] and theoretically[36–38] that the source of nonexponential kinetics of a tagged hydrogen bond in water at all temperatures, including the supercooled regime is not due to correlations between different hydrogen bonds, it is unclear why the distribution of hydrogen bond lifetimes can have anything else but an exponential long time decay. Furthermore, it has been found that the mean hydrogen bond lifetimes, obtained from the distributions, showed an Arrhenius temperature dependence,[32,34] approximately Arrhenius temperature dependence,[39] as well as a power-law behavior,[33] which was related to the ''Angell'' temperature of water.[40]

It is obvious from the above historic overview that it is desirable to put the various treatments in perspective and to clarify the effects of the choice of H bond *and* HB lifetime definition on the simulated bond dynamics. A major focus of this paper it to make these clarifications by establishing connections between different approaches and thus to provide a coherent picture of the dynamic behavior of H bonds in liquid water. In order to succeed, explicit analytical relations between functions like ''distribution of HB lifetimes'' and ''intermittent H bond correlation functions'' have to be established.

The rest of the paper is organized as follows: In Sec. II we give an overview of the reactive flux correlation function formalism for the calculations of rate constants and discuss its relation to methods introduced by Rapaport[16] and Stillinger[15] to study distinct lifetime queries. We quickly restate the pertinent results of reactive flux calculations in the case of water:[27] the phenomenological model allows us to identify the elementary processes governing HB dynamics and to understand what physical processes affect the qualitative dynamic behavior of water. Section II provides analytical relations between different ''continuum'' HB correlation functions, as well as between ''continuum'' and ''intermittent'' HB correlation functions. Specifically, we establish relations between different probability densities, and provide the identity between average continuum HB lifetime and the inverse of transition state theory (TST)[41] rate constant. Further, we establish the relation between first passage time probability densities for bond breaking and bond reforming events and reactive flux function. In Sec. IV we present computer simulation results of all the quantities defined in the preceding section for SPC water[42] at room temperature. We compare them with analytical predictions, that are completely general. Irrespective of H bond criteria used in the simulation, our analysis and computations reveal exponential distribution of HB lifetimes and establish its Arrhenius temperature dependence. In the last section we summarize the most important finding.

II. RELAXATION RATE CONSTANTS AND TIME CORRELATION FUNCTIONS

We define a HB correlation function $c(t)$:[25,26]

$$c(t)=\frac{\langle h(0)h(t)\rangle}{\langle h\rangle}, \tag{1}$$

where the dynamical variable $h(t)$ equals unity, if the particular *tagged* pair of molecules is hydrogen bonded, and is zero otherwise. The set of values $h(t)$ for all pairs of molecules completely specifies the bond organization at a given instant. The average number of H bonds in an equilibrium of N water molecules is equal to the number of all pairs, multiplied by the average value of the H bond population operator, $\frac{1}{2}N(N-1)\langle h\rangle$. For very long time t, $c(t)$ approaches $\langle h\rangle \sim 1/\langle N\rangle \sim 0$. $c(t)$ is the conditional probability that the hydrogen bond between a tagged pair of water molecules is intact at time $t, h(t)=1$, given the bond was intact at time zero, $h(0)=1$. Note that by construction, $c(t)$ measures correlations in a time series of bonds independent of possible bond breaking events. Therefore it is the ''intermittent HB correlation function'' introduced by Rapaport.[16] Onsager's regression hypothesis[43] states that in the linear regime, the time evolution of $c(t)$ obeys:

$$\frac{\overline{\delta h}(t)}{\overline{\delta h}(0)}=\frac{c(t)-c(\infty)}{c(0)-c(\infty)}\simeq c(t), \tag{2}$$

where $\overline{\delta h}(t)=\overline{h}(t)-\langle h\rangle$, and the overbar average is a nonequilibrium average. This expression embodies the idea that for systems close to equilibrium one cannot distinguish between spontaneous fluctuations and deviations from equilibrium that are externally prepared.

The rate of relaxation to equilibrium is characterized by the reactive flux HB correlation function, $k(t)$:[25,26]

$$k(t)\equiv\frac{-dc(t)}{dt}=\frac{\langle\dot{h}(0)h(t)\rangle}{\langle h\rangle}=-\frac{\langle\dot{h}(0)[1-h(t)]\rangle}{\langle h\rangle}, \tag{3}$$

where the overdots denote the time derivative. The last expression in Eq. (3) follows because $\langle h(0)\dot{h}(t)\rangle=-\langle\dot{h}(0)h(t)\rangle$ and $\langle\dot{h}(0)\rangle=0$. $-k(t)$ measures the average rate of change of hydrogen bond population (initial set of hydrogen bonds) for those trajectories where the bond between a tagged pair of molecules is broken at a time t later.

To calculate the H bond relaxation times in water, we make connection between microscopic H bond dynamics and the phenomenological description of the reaction, e.g., H bond breaking/reforming:

$$A\underset{k'}{\overset{k}{\rightleftarrows}}B \tag{4}$$

with k and k' as the forward and backward rate constants, respectively. The relaxation to equilibrium occurs as the system undergoes several transitions from reactants, A (H bond ON, i.e., $\langle h\rangle$) to products, B (H bond OFF, i.e., $1-\langle h\rangle$). To the extent that each H bond acts independently of other H bonds, i.e., subsequent recrossings are uncorrelated,[37,38] these transitions are expected to be Poissonian. Accordingly, after the initial transitory period, $\overline{\delta h}(t)$ should decay exponentially,

$$\overline{\delta h}(t)\sim\overline{\delta h}(0)e^{-t/\tau}, \tag{5}$$

where the reaction time constant $\tau=(k+k')^{-1}$. τ characterizes the transition of the system from state A (bond ON) to state B (bond OFF). According to detailed balance condition,

$$\frac{1-\langle h\rangle}{\langle h\rangle}=\frac{k}{k'}, \tag{6}$$

and therefore the characteristic relaxation time τ is related to the rate constant for breaking an H bond, k, through

$$\tau=\frac{1-\langle h\rangle}{k}, \tag{7}$$

where the total population is constant, i.e., $\langle h\rangle+(1-\langle h\rangle)=1$.

To the extent that the above phenomenology, i.e., first order kinetics, is accurate, we get the connection between the rate constant for H bond breaking, k, or equivalently, the average HB lifetime, $\tau_{\mathrm{HB}}=1/k$, and the time correlation function $k(t)$, which is valid for times longer than the initial time decay, i.e., transient time t_{trans}:

$$k(t)=-\frac{\langle\dot{h}(0)[1-h(t)]\rangle}{\langle h\rangle}\sim ke^{-kt},\quad t>t_{\mathrm{trans}}. \tag{8}$$

For all trajectories that are passing the transition point in the reactive direction (H bond breaking) and end up in the product state (H bond OFF) for a long time and never *re*cross the transition state (H bond *re*forming), $k\sim k(0^+)=k_{\mathrm{TST}}$.[44] In that case we obtain the TST estimate of the rate of relaxation.[41] Accordingly, $1/k_{\mathrm{TST}}$ represents the ''continuum'' τ_{HB}. In contrast with the TST approximation that does not allow recrossings, some percentage of trajectories may cross the dividing surface more than once during the transition between reactant and product states. This recrossing transient relaxation dynamics reduces $k(t)$ from $k(0^+)$. It is conventional to express the reduction of $k(t)$ due to recrossings in terms of the time dependent dynamical transmission coefficient, $\kappa(t)$, defined as

$$\kappa(t)=\frac{k(t)}{k(0^+)} \tag{9}$$

which essentially measures the fraction of trajectories that are stabilized in the state to which they are initially directed. Accordingly, while k_{TST} estimate is a purely static quantity depending mainly on the probability of finding the system at the dividing surface, $\kappa(t)$ depends upon very fast transient relaxation dynamics. While the value of a rate constant estimated from TST does depend on the choice of the population operator that determines the location of the dividing surface, the reactive flux method ensures that the actual dynamical forward rate constant, k, i.e., the product $\kappa\times k_{\mathrm{TST}}$, is independent of the precise choice of the population operator and transition state.[45]

Thus far we have assumed that the rate constants for hydrogen bond breaking and making are well defined, or equivalently, that relaxation from a nonequilibrium H bonded state is exponential in time, Eq. (5). The reactive flux correlation functions, $k(t)$, in water at different temperatures, that we have computed,[27,37,38] (see also Fig. 8), however, do not relax exponentially (do not sattle to a plateau after an initial transient time). Beyond the transient time, the slopes of $\log k(t)$'s increase (decrease in absolute values) monotonically with time. Therefore we have to rethink the appropriate phenomenology or kinetic model for our process under consideration, i.e., breaking and making of hydrogen bonds in water. In other words, we have to redefine the states in Eq. (4), in order to be able to successfully interpret the relaxation of $k(t)$. Equation (4) implies the division of tagged pairs to bonded (A), and nonbonded (B). In the following, we limit the definition of the product, B, to nonbonded pairs that were initially bonded and whose molecules remain within the first coordination shell of each other. Denoting the populations of A and B by $c(t)$ and $n(t)$, the reaction kinetics is described by[27]

$$k(t)=kc(t)-k'n(t). \tag{10}$$

In this formulation, $n(t)$ represents a measure of *local* strain in the H bond network. It is determined from $n(t)=\int_0^t dt'\,k_{in}(t')$, where $k_{in}(t)=-\langle\dot{h}(0)[1-h(t)]H(t)\rangle/\langle h\rangle$ is the restrictive reactive flux function, with

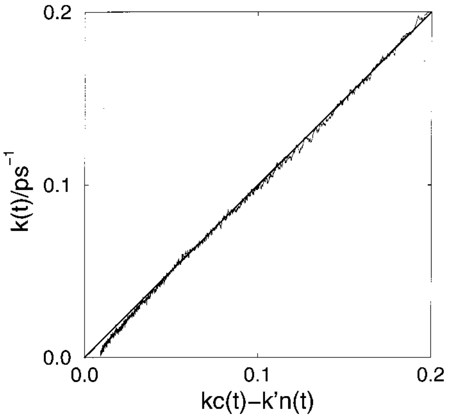

FIG. 1. The validity of Eq. (10) in the main text is judged by comparing the simulation data (jagged line) with the straight line of unit slope. The values of the rate constants k and k' for SPC water at $T=300$ K used in the plot are 0.6 ps^{-1} and 0.9 ps^{-1}, respectively (their values differ from those in Ref. 27, where T was 312 K).

$$H(t)=\begin{cases}1 & \text{if } R_{\mathrm{OO}}(t)<R_{\mathrm{OO}}^{c}\\ 0 & \text{otherwise.}\end{cases}$$

$R_{\mathrm{OO}}(t)$ is the distance between the oxygen atoms of a tagged pair and R_{OO}^{c} is its cutoff value, 3.5 Å. In analogy with experiments (e.g., neutron scattering[2]) that measure the movement of an H atom that depends only on its local environment (a small region between the two oxygen atoms) we consider only pairs of water molecules that remain *able* to form a bond. The probabilities $c(t)$ and $n(t)$ therefore correspond to local populations that interconvert in the first coordination shell of water molecules according to the simplest first order kinetics [Eq. (10)]. Only one combination of phenomenological rate constants for breaking and reforming H bonds, k and k' gives the indentity curve, i.e., $k(t)/[kc(t)-k'n(t)]$ vs t gives us a plateau, Fig. 1. The total population, i.e., $c(t)+n(t)$, however, is *not* constant [as in Eqs. (6) and (7)], the reason being that $n(t)$ relaxes not only by conversion back to the bonded state, but is also depleted because of the diffusion process.[27] Phenomenology which accounts for the coupling between H bond kinetics of breaking and reforming of H bonds and translational diffusion, successfully interprets molecular dynamics results for $k(t)$, $n(t)$.[27] We treat relaxation kinetics using diffusion equation with *source* and *sink* terms as in reaction–diffusion systems:[27,46]

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t)=D\nabla^{2}\rho(\mathbf{r},t)+\delta(\mathbf{r})kc(t)-\delta(\mathbf{r})k'n(t)$$
$$\equiv D\nabla^{2}\rho(\mathbf{r},t)-\frac{dc(t)}{dt}\delta(\mathbf{r}). \tag{11}$$

Density of the diffusing unbonded pair, $\rho(\mathbf{r},t)$, changes in space and time according to Fick's law of diffusion, where D is the interdiffusion constant of the pair. In addition, we have to take into account that in the nearest neighbor region the concentration of diffusing and nondiffusing species changes as bonds form and break. Delta function in Eq. (11) localizes $\mathbf{r}$, the vector between the pair, to within a volume a^{3}, where a is the range of widths over which a nearest neighbor might move without breaking the H bond. Therefore

$$\rho(0,t)=\frac{n(t)}{a^{3}} \tag{12}$$

$\delta(\mathbf{r})$ corresponds to the region of space where both diffusing and nondiffusing species coexist, and therefore they can interconvert. And we have already established that they interconvert at $\mathbf{r}\leqslant a$ according to the simple kinetics [Eq. (10)]. The model was solved through Fourier and Laplace transformations in space and time, respectively. The spatial resolution of Eqs. (11) and (12) requires regularization. Hence, the solution depends upon a wave vector cutoff, $q_{c}=(6\pi^{2})^{1/3}/a$. The solution gives the Laplace transform of $k(t)$ as

$$\tilde{k}(s)=\frac{k}{s+k+k'sf(s)}, \tag{13}$$

where

$$f(s)=3\tau_{d}\left[1-\sqrt{s\tau_{d}}\arctan\frac{1}{\sqrt{s\tau_{d}}}\right] \tag{14}$$

with $\tau_{d}^{-1}=Dq_{c}^{2}$. Note that in the limit of large s, i.e., times that are small compared to τ_{d}^{-1}, $f(s)\approx 1/s$, so that

$$\tilde{k}(s)\sim\frac{k}{s+k+k'}. \tag{15}$$

In the limit of large τ_{d}, i.e., slow diffusion, the predictions therefore approach the result of single exponential kinetics, with rate constant $k+k'$:[47]

$$k(t)\sim ke^{-(k+k')t}. \tag{16}$$

This fact may also be verified from dimensional analysis of Eq. (11) leading to $n(t)+c(t)=\text{const}$. For water, however, τ_{d} is not large.[27] The self-diffusion constant is larger than $10^{-5}\,\mathrm{cm}^{2}\,\mathrm{s}^{-1}$, and a, approximately the radius of a water molecule, is ∼1.5 Å. These numbers show that τ_{d} is below 1 ps for water at standard conditions, the value that is comparable to $1/k$ and $1/k'$.[27]

III. ANALYTICAL RELATIONS

A. Continuum world: Probability densities of first passage times

In this section we analyze two probability densities, that are used in the literature to compute ''continuum HB lifetimes.'' We stress the distinctions and provide connections between the two functions.

Let us define a *survival probability* for a *newly generated bond*, $s(t)$, as conditional probability the bond between a tagged pair of molecules is ON at time t, given the bond was formed for the last time at $t=0$. Its time derivate represents the *first passage time probability density* of H bonds, $P(t)=-ds(t)/dt$. $P(t)$ is usually loosely called ''probability distribution of HB lifetimes,''[33–35] or ''histogram of HB lifetimes.''[32,48] The H bond population operator, h, defined in Sec. II, in such a case equals unity if a bond between a tagged pair of molecules is *continuously* ON, and is zero otherwise. Therefore,

$$P(t)=\frac{\langle[1-h(0)]\delta[t-\int_0^t h(t')dt'][1-h(t)]\rangle}{\langle 1-h(0)\rangle}, \tag{17}$$

where $\langle\cdots\rangle$ denotes the average over all bonds *created* at $t=0$.

The mean first passage time (MFPT) for newly formed bonds, i.e., the mean HB lifetime, $\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle$, is then calculated from

$$\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle=\int_0^\infty s(t)dt=\int_0^\infty tP(t)dt, \tag{18}$$

where average is taken over all bonds that ever existed.

Let $c_c(t)$ be the conditional probability a randomly picked bond between a tagged pair of molecules is ON at time *t*, given the bond was ON *at all times* between zero and *t*. It is a *survival probability* for an *average bond*. It differs from $s(t)$ in that we relax the condition of bond formation at $t=0$. Note that by construction this probability represents the ''continuum HB correlation function'' introduced by Rapaport[16] (see Sec. I). Its time derivative, $p(t)=-dc_c(t)/dt$, is again the first passage time probability density of H bonds, however in this case it represents the probability distribution of *life expectancies*, i.e., *persistence times:*

$$p(t)=\left\langle\delta\left[t-\int_0^t h(t')dt'\right][1-h(t)]\right\rangle, \tag{19}$$

where $\langle\cdots\rangle$ denotes the average over all bonds *present* at $t=0$.

The MFPT averaged over initial states, i.e., the mean H bond life expectancy for all bonds present at a particular time $t,\langle\tau_{\mathrm{ex}}\rangle$, is then calculated from

$$\langle\tau_{\mathrm{ex}}\rangle=\int_0^\infty c_c(t)dt=\int_0^\infty tp(t)dt, \tag{20}$$

where average is taken over all bonds that were present at $t=0$. This time is also identified as mean HB persistence time, or a continuous survival time constant.[19]

What is the relation between $P(t)$ and $p(t)$? For the moment we restrict ourselves to the Markovian process, where the future of the hydrogen bond population operator, $h(t)$, depends only on its present state, not on its past. In other words, probability $p(t)dt$ that $h(t)$ has its first ''blip'' between t and $t+dt$ [assuming $h(0)=1$] does not depend on the values of $h(t)$ for $t<0$. In this case it follows from Eqs. (17) and (19) that $P(t)=p(t)$.

The general relation (in the case of non-Markovian stochastic dynamics) between the two probability densities goes as follows: Probability of finding a bond with lifetime *t* in an arbitrary trial is $\propto t^*P(t)$. If finding such a bond, it can happen to be at any age within the interval $0<A<t$. Probability to be at particular age $A'\propto 1/t$ (there are *t* possibilities). Hence, the probability of selecting a bond with lifetime *t and* current age A' will be proportional to $t^*P(t)^*1/t=P(t)$ unless $A'>t$. Of course, $P(t)$ drops to zero for $A'>t$. Thus,

$$p(t')\propto\int_0^\infty P(t)\Theta(t-t')dt=\int_{t'}^\infty P(t)dt, \tag{21}$$

where Θ is the Heaviside step function.

Equation (21), rewritten as $p(t)\propto\int_t^\infty P(t')dt'$ still needs normalization such that $\int_0^\infty p(t)dt=1$. Hence,

$$p(t)=\frac{\int_t^\infty P(t')dt'}{\int_0^\infty dt\int_t^\infty P(t')dt'}. \tag{22}$$

The above equation establishes a general relation between the two first passage time probability densities, $P(t')$ with a fixed starting point, and $p(t)$ with a starting point averaged over all pairs bonded at any particular time.

In the limit of $t=0^+$, Eq. (22) reads

$$p(0^+)=1\bigg/\int_0^\infty dt\int_t^\infty P(t')dt'. \tag{23}$$

Integration by parts of the denominator of Eq. (23) gives

$$p(0^+)=1\bigg/\int_0^\infty tP(t)dt\equiv 1/\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle. \tag{24}$$

Because of the equality

$$p(0^+)=\lim_{t\to 0^+}-\frac{dc_c(t)}{dt}=-\frac{dc(t)}{dt}\Big|_{t=0^+}\equiv k(0^+)\equiv k_{\mathrm{TST}}, \tag{25}$$

it follows that

$$\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle=\frac{1}{k_{\mathrm{TST}}}. \tag{26}$$

This result agrees with recently derived indentity between a Kramers-type escape rate and the inverse of the associated mean first passage time (MFPT) valid for a completely general system.[49] For the special case of H bond dynamics, its validity is reaffirmed by our numerical results shown later in the text.

B. Reactive flux in terms of first passage time probability densities

How can we study an intermittent function like $c(t)$, and its derivative, $k(t)$, in terms of continuous functions, i.e., probability densities, defined in the preceding section? This can be done by representing an average trajectory that contributes to $k(t)$ as a sequence of consecutive continuous events. In order to do that we first introduce a function symmetric to $P(t)$, as follows.

Let $s'(t)$ be a conditional probability the bond between a tagged pair of molecules is OFF at time *t*, given the bond ruptured for the last time at $t=0$. Its time derivative, $Q(t)=-ds'(t)/dt$, is the probability density of first reforming for bonds that broke at $t=0$. Loosely speaking again, this would correspond to a ''probability distribution of death times.''

The relation for $k(t)$ follows:

$$k(t)=p(t)-\int P(t_1)Q(t-t_1)dt_1 +\int P(t_1)Q(t_2-t_1)P(t-t_2)dt_1\,dt_2 -\int P(t_1)Q(t_2-t_1)P(t_3-t_2) \times Q(t-t_3)dt_1\,dt_2\,dt_3+\cdots. \tag{27}$$

It is useful to rewrite Eq. (27) in terms of the Laplace transforms, $\tilde{y}(s)\equiv\int_0^\infty y(t)e^{-st}\,dt$:

$$\tilde{k}(s)=\tilde{p}(s)-\tilde{P}(s)\tilde{Q}(s)+\tilde{P}(s)\tilde{Q}(s)\tilde{P}(s) -\tilde{P}(s)\tilde{Q}(s)\tilde{P}(s)\tilde{Q}(s)+\cdots. \tag{28}$$

Equation (28) is a geometric series, yielding

$$\tilde{k}(s)=\frac{\tilde{p}(s)[1-\tilde{Q}(s)]}{1-\tilde{P}(s)\tilde{Q}(s)}. \tag{29}$$

We can express $\tilde{p}(s)$ as a functional of $\tilde{P}(s)$:

$$\tilde{p}(s)=\frac{1}{\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle}\int_0^\infty e^{-t_1 s}\,dt_1\int_{t_1}^\infty P(t)dt. \tag{30}$$

Integration by parts gives

$$\tilde{p}(s)=\frac{1-\tilde{P}(s)}{\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle s}. \tag{31}$$

Hence, Eq. (29) reads

$$\tilde{k}(s)=\frac{[1-\tilde{P}(s)][1-\tilde{Q}(s)]}{\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle s[1-\tilde{P}(s)\tilde{Q}(s)]}. \tag{32}$$

In the limit of large *s*, i.e., small *t* limit, we get

$$\lim_{s\to\infty}\tilde{k}(s)=\frac{1}{\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle s} \tag{33}$$

which coincides with Eqs. (25) and (26).

At this point it is useful to examine an application of Eq. (32) for a simple case. Assuming that $P(t)$ and $Q(t)$ decay as single exponential functions, with relaxation times τ, and σ, $P(t)=(1/\tau)e^{-t/\tau}$, $Q(t)=(1/\sigma)e^{-t/\sigma}$, one obtains in Laplace transform representation

$$\tilde{P}(s)=\frac{1}{s\tau+1},\quad \tilde{Q}(s)=\frac{1}{s\sigma+1}. \tag{34}$$

In this special case where librations are coarse grained out it follows from Eq. (31) that $\tilde{p}(s)=\tilde{P}(s)$, and by using Eq. (29), we get

$$\tilde{k}(s)=\frac{1}{\tau\left(s+\dfrac{1}{\tau}+\dfrac{1}{\sigma}\right)}. \tag{35}$$

Within the above assumptions, one can equate $1/\tau=k$ and $1/\sigma=k'$, where k and k' are rate constants for breaking and reforming an H bond introduced in Sec. II. We recover the result pertaining to two-state phenomenology for $c(t)$, Eqs. (4)–(6):

$$c(t)=[1-\langle h\rangle]e^{-(k+k')t}+\langle h\rangle, \tag{36}$$

with the initial condition $h(0)=1$, and the detailed balance condition $(1-\langle h\rangle)/\langle h\rangle=k/k'$, Eq. (6). As discussed in Sec. II, this phenomenology is not correct, however, for any noninfinite diffusion. That is, it is not correct for the realistic case with finite diffusion leading to an ultimate value of $\langle h\rangle\sim0$. [Exponential relaxation for $k(t)$, Eq. (15), is obtained from Eq. (13) only in the limit of $D\to0$.]

$k(t)$ is a functional of $P(t)$ and $Q(t)$. From the present analysis it is obvious that functions $k(t)$ and $c(t)$ ($\tilde{c}(s)=[1-\tilde{k}(s)]/s$), would decay exponentially if, and only if *both* probability densities $P(t)$ and $Q(t)$ were also exponential. Only in this case do Eqs. (34) and (35) apply. In view of insignificant inter-hydrogen bond correlations demonstrated in a separate work,[37,38] $P(t)$ has to be exponential by construction, as it represents a continuous elementary process of breaking a bond. Indeed, in the next section we show it is not $P(t)$ that makes functions like $c(t)$ and $k(t)$ nonexponential. It is $Q(t)$.

IV. NUMERICAL RESULTS

A. Computer simulation details

To evaluate the influence of different HB definitions in a simulation on all HB correlation functions that we have defined in the preceding sections, we choose to use two definitions based on geometric criteria. To speed up the procedure, in both cases we first discard all pairs with oxygen–oxygen distance larger than $R_{\mathrm{OO}}=3.5$ Å.[27,37,47] The remaining tagged pairs with two water molecules separated by less than 3.5 Å can be either bonded or not bonded depending upon their distance between an oxygen atom acting as a proton acceptor and a hydrogen of the molecule whose oxygen atom acts as a proton donor, i.e., OH intermolecular distances, R_{OH}, and the angle between O–O distance and the covalent O–H bond, ϕ^c.[9,25,27,37,47] In one definition, we use the following cutoff values:[25,27,37,47] $R_{\mathrm{OH}}^c=2.45$ Å, which corresponds to the first minimum in the corresponding radial distribution function for SPC water,[42] and $\Theta^c=\pi/6=30°$, an angle at which the average number of H bonds per water molecule, $\langle n_{\mathrm{HB}}\rangle$ is within 10% of the asymptotic value for large ϕ^c, Fig. 3.

We choose the pertinent second set of cutoff values for R_{OH}^c and Θ^c, which determine the optimal dividing surface, according to the following argument: as discussed in Sec. II, because TST does not take into account recrossings, it is always an upper bound to the true rate constant, k. For this reason, the best choice for a transition state surface is obviously the one which predicts the lowest k_{TST}. Variational transition state theory (VTST)[51,52] minimizes the recrossing effects by effectively moving the dividing surface along the minimum energy paths between reactants and products.[53] Figures 2 and 3 illustrate how the value of k_{TST} changes upon separately varying the parameters that define our dividing surface, i.e., R_{OH}^c, and Θ^c. Only the set of parameters

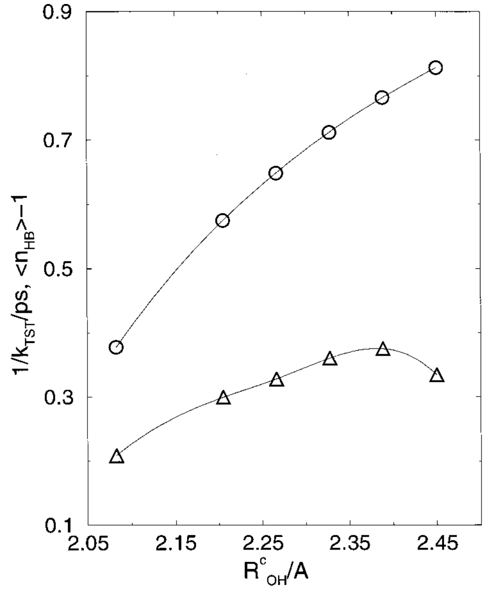

FIG. 2. Dependence of the inverse of the TST rate constant, $1/k_{\mathrm{TST}}$ (triangles), and the average number of H bonds per water molecule, $\langle n_{\mathrm{HB}}\rangle$ (circles), on cutoff values of the intermolecular OH distance, R^c_{OH}. Both quantities are drawn for $\phi^c=40°$. Lines are guides to the eye.

that gives the lowest value of k_{TST} is presented in both figures. We find an extremum in the first curve (Fig. 2), but not in the other, Fig. 3. Plausible explanation for the maximum in $1/k_{\mathrm{TST}}$ as a function of the intermolecular OH distance would be that there are two opposing effects: it is harder to break a bond if R_{OH} is assigned a bigger value, but the number of bonds available to breaking increase with R_{OH}. Notice how $\langle n_{\mathrm{HB}}\rangle$ increases monotonically with intermolecular OH distance. However, we observe no maximum in the angle dependence of $1/k_{\mathrm{TST}}$. Instead, an asymptotic value is reached at ~40° for all values of R^c_{OH} (not shown here) as water molecules do not prefer big angles (even if allowed) because H bonds are so directional. Notice that in this case the average number of bonds per molecule reaches the asymptotic value at ~40°. According to these results, we choose $R^c_{\mathrm{OH}}=2.39$ Å, and $\Theta^c=40°$. This choice of cutoff parameters leads to a somewhat higher value of $\langle n_{\mathrm{HB}}\rangle$, which coincides with the result obtained by using the energetic criterion for H bond in SPC water.[50] For the remainder of this paper we will refer to the first definition as ''stricter,'' and to the second as ''less strict.''

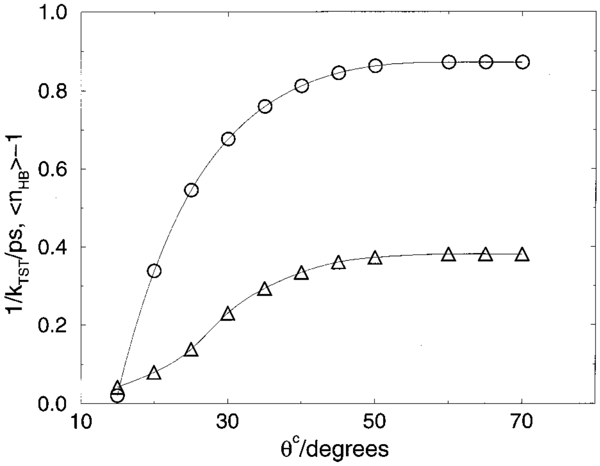

FIG. 3. Dependence of the inverse of the TST rate constant, $1/k_{\mathrm{TST}}$ (triangles), and the average number of H bonds per water molecule, $\langle n_{\mathrm{HB}}\rangle$ (circles), on cutoff angle, Θ^c. Both quantities are drawn for $R^c_{\mathrm{OH}}=2.45$ Å. Lines are guides to the eye.

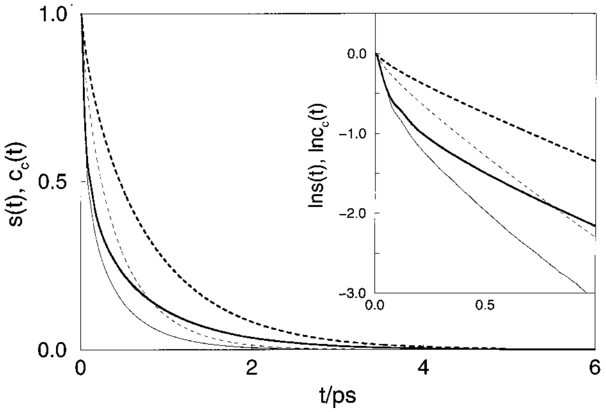

FIG. 4. Survival probabilities for a newly generated bond, $s(t)$ (solid lines) and for an average bond, $c_c(t)$ (dashed lines), for stricter HB definition (thin lines) and for less strict HB definition (thick lines). Inset represents the short time behavior of all functions on a semilog plot.

We performed classical MD simulations in NVE ensemble with 250 SPC water molecules at fixed density 1.0 g/cm^3 and $T=300$ K. We choose SPC over SPC/E (Ref. 54) model because we intend to extend our studies to solutions and interfacial systems where SPC is known to out-perform its successor.[55] Nosé–Hoover thermostat was used to control the temperature during the equilibration time. When calculating dynamical properties we switched off the thermostat to ensure purely Newtonian dynamics. The equations of motions were integrated using velocity predictor–corrector method with a time step of 0.5 fs. Energy drift was 0.0023 kJ/mol per ps, which represents only 0.005% of the total energy. Periodic boundary conditions were used together with the minimum image convention for non-Coulombic interactions. Ewald summation technique was applied to evaluate the long-range Coulomb forces. Time derivatives of the hydrogen bond correlation functions were calculated every time step. The reason for this choice is that we have established by trial and error procedure that we are leaving out some ''hot'' trajectories if we are calculating the derivative only every 5 fs or 10 fs, the consequence being higher values of these functions at longer times. This trend, going from 1 fs to 2 fs, 5 fs and 10 fs seems consistent. For studying the long time relaxation, we computed the correlation functions out to times several orders of magnitude longer than their transient times.

B. Discussion

The conditional probabilities, $s(t)$ and $c_c(t)$, for both HB definitions are presented in Fig. 4. Note that the $s(t)$ functions show a glitch within a short transient time (more visible on a semilog plot). It reflects the librational motion of a proton in a cage.[56] Because this motion is an oscillatory function, it cannot give an exponential relaxation at all shorter times from zero on. In all cases, we observe a rapid

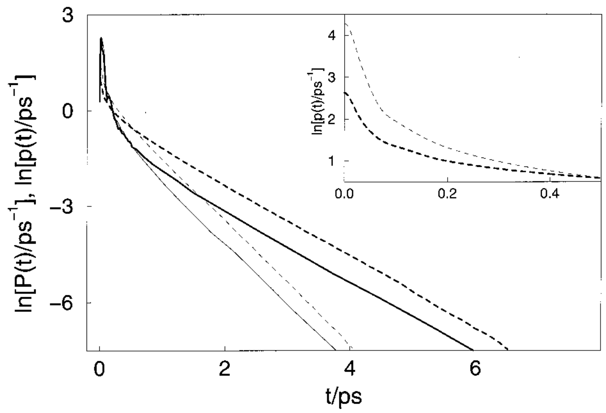

FIG. 5. Comparison between first passage time probability densities of H bonds, $P(t)$ (solid lines), and $p(t)$ (dashed lines), for stricter HB definition (thin lines) and for less strict HB definition (thick lines). All on semilog plot. Inset shows the transient behavior of $p(t)$ for both definitions.

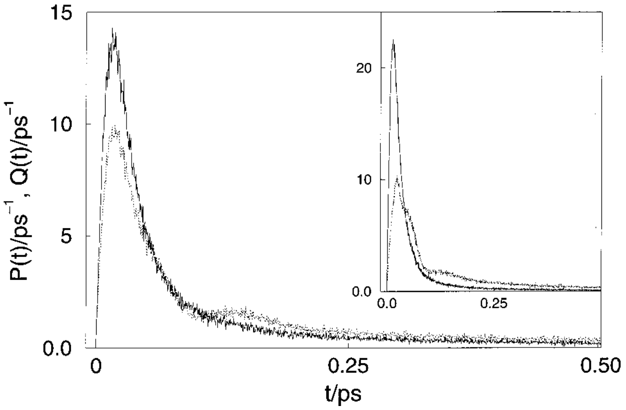

FIG. 6. Comparison between transient behaviors of first passage time probability densities for bonds that are created at $t=0$, $P(t)$ (solid lines), and for first reforming for bonds broken at $t=0$, $Q(t)$ (dotted lines). The major graph is for less strict HB definition, the inset for the stricter HB definition.

initial decay in the correlation function due to the fast vibrational motion. This effect is, however, much weaker in the case of $c_c(t)$ which describes the decay of bonds randomly selected regardless of their actual age. A somewhat slower overall decay of $c_c(t)$ is explained by the fact that long-lived bonds are more probable to pick and hence contribute more to the average. $s(t)$, on the other hand, is number-averaged, so short-lived bonds contribute equally. As expected, less strict HB definition gives a considerably slower decay of correlation functions.

Figure 5 shows the derivatives of these functions, i.e., $P(t)$ and $p(t)$. In the limit of $t\rightarrow 0^+$, both functions behave as expected. Most bonds form through libration like motion which makes immediate rupture unlikely. Therefore, $P(0^+)=0$ (Fig. 6). $p(0^+)=k_{\mathrm{TST}}$ (Fig. 5, inset), as required by Eq. (25). Note that $P(t)=p(t)$ in this limit only if the librations are coarse-grained out. $P(t)$ and $p(t)$ are exponential after the transient time (that manifest librations). Because of relation given in Eq. (22), both semilog functions should have the same slope, and Fig. 5 confirms that indeed they do. For the stricter HB definition, we find $P(t)=Ae^{-t/\tau}$, $\tau=0.5\,\mathrm{ps}$, $A=1/1\,\mathrm{ps}$; and $p(t)=A'e^{-t/\tau}$, $\tau=0.5\,\mathrm{ps}$, $A'=1/0.65\,\mathrm{ps}$. The numerical results show that the functional form of $P(t)=p(t)=(1/\tau)e^{-t/\tau}$ adopted in Eq. (34) does not hold for water because of librations that contribute to the decay of these functions. Thus, τ differs from $1/k$ (Table I). Assumptions made in Eqs. (34) and (35) do not apply because transient dynamics makes a significant but different

TABLE I. Comparison between the characteristic H bond times determined from different approaches, for both HB definitions used in the simulations. t_{int} denotes the range of integration, and t_{sim} the length of simulation runs. (C): $1/k_{\mathrm{TST}}=\langle N\rangle t_{\mathrm{sim}}/n_r$, $t_{\mathrm{sim}}\geqslant 1$ ps, where n_r is the number of ruptures. In the limit of $\nu\rightarrow 0$ (where ν is the sampling frequency) it can be shown that TST definition of rate constant and that determined from the number of barrier crossings are identical. (F): $\tau^i=\langle N\rangle t_{\mathrm{sim}}/n_w$, where n_w is the number of all pairs that ever had a bond between $t=0$ and $t=t_{\mathrm{sim}}$. (G): ''Zero frequency part of $c(t)$'': $\langle\tau^i\rangle=\int_0^\infty c(t)dt$, $\hat{c}(0)=\tau^i$. Symbols in (A), (B), (D), (E), and (H) are explained within the main text.

Characteristic HB time	Hydrogen bond times/ps	
	Stricter HB definition	Less strict HB definition
(A) $\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle$, Eq. (20)	0.18, $t_{\mathrm{int}}=7$ ps	0.35, $t_{\mathrm{int}}=7$ ps
	0.23, $t_{\mathrm{int}}=50$ ps	0.38, $t_{\mathrm{int}}=50$ ps
	0.24, $t_{\mathrm{int}}=250$ ps	0.39, $t_{\mathrm{int}}=250$ ps
(B) $1/k_{\mathrm{TST}}, k(0^+)$	0.23	0.38
(C) $1/k_{\mathrm{TST}}$, direct counting	0.23	0.38
(D) $\langle\tau_{\mathrm{ex}}\rangle$, Eq. (22)	0.37, $t_{\mathrm{int}}=7$ ps	0.63, $t_{\mathrm{int}}=7$ ps
	0.41, $t_{\mathrm{int}}=50$ ps	0.74, $t_{\mathrm{int}}=50$ ps
	0.43, $t_{\mathrm{int}}=250$ ps	0.75, $t_{\mathrm{int}}=250$ ps
(E) τ, slope of $\ln p(t)$, or $\ln P(t)$, $t>t_{\mathrm{trans}}$	0.5	0.85
(F) τ^i, direct counting	2.1, $t_{\mathrm{sim}}=20$ ps	2.2, $t_{\mathrm{sim}}=20$ ps
	2.86 ± 0.03, $t_{\mathrm{sim}}=50$ ps	2.95 ± 0.03, $t_{\mathrm{sim}}=50$ ps
	4.83, $t_{\mathrm{sim}}=250$ ps	5.01, $t_{\mathrm{sim}}=250$ ps
(G) Zero frequency part of $c(t)$	4.4, $t_{\mathrm{int}}=50$ ps	4.7, $t_{\mathrm{int}}=50$ ps
(H) $1/\tau_{\mathrm{HB}}=1/k$, Eq. (10)	1.6 ± 0.16	1.6 ± 0.16

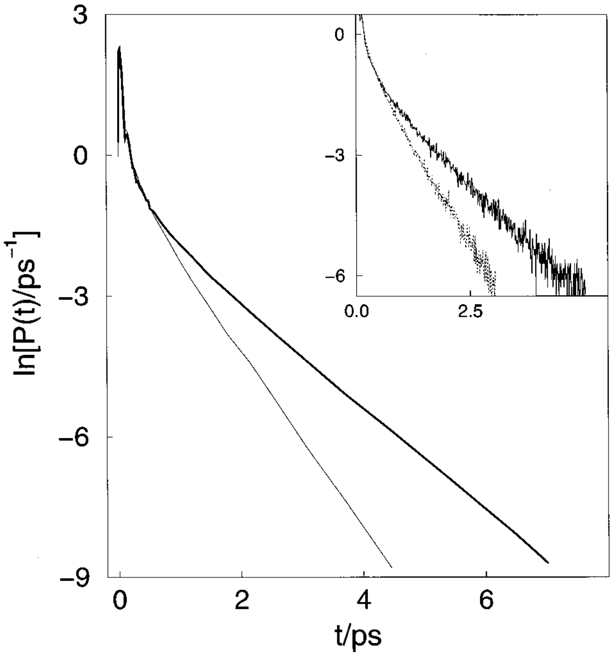

FIG. 7. Semilog plots of the long time behavior of first passage time probability densities of H bonds, $P(t)$. Thin line is for stricter HB definition, thick one for less strict HB definition. The smooth curves were obtained from raw data (shown in the inset) by merging results over progressively increasing time intervals.

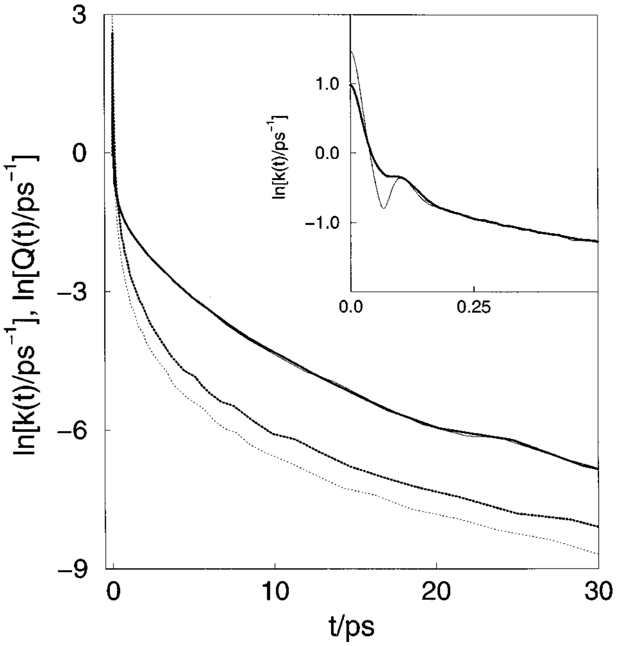

FIG. 8. Comparison between the long time behavior of the HB reactive flux functions, $k(t)$ (solid curves) and the first passage time probability densities for reforming of bonds that are broken at $t=0$, $Q(t)$ (dotted curves). All on semilog plot, and for stricter HB definition (thin), and less strict HB definition (thick). The inset shows transient behavior of $k(t)$ (on semilog plot) for both HB definition. Note that with less strict HB definition (thick line) the hump at around 70 fs almost disappears, due to a bigger cutoff angle ϕ^c which manifests reduced sensitivity to bond bending within several librational periods. The smooth curves were obtained from raw data as noted with Fig. 7.

contribution to $k(t)$ and to $P(t)$. Note the qualitative differences in transient times: while $k(t)$ decays from the very beginning,[27,37,38] (see also inset of Fig. 8), $P(t)$ goes through a maximum at a time related to a librational period, Fig. 6.

Figure 6 compares the probability densities $P(t)$ and $Q(t)$ at short times. As expected, $Q(t)$ displays a maximum at approximately the same position as $P(t)$, i.e., librational periods for breaking and reforming a bond do not differ appreciably. The small differences that we do notice with a stricter HB definition are attributed to anharmonicity of bond interaction. Note that $Q(t)$ is not the probability of reforming but rather the probability density for a bond which is known to reform. Only bonds that do reform are included in the statistics with $Q(t)$ showing how quickly a bond reforms, if it does at all. The distribution includes a notable fraction of reforming times below 20 fs. This is why it is important to use sampling intervals well below 10 fs.

After the transient time, $P(t)$ has an exponential decay, as it measures an elementary process of having a bond continuously ON, so no diffusion can take place. We are looking at a pair and a bond in between, but at the same time other molecules diffuse around, i.e., environment is changing in time. However, if the environment would have any appreciable effect on the decay of $P(t)$, this would contradict what we actually observe,[37,38] namely that static and dynamic correlations with fluctuations of neighboring bonds in water above and below room temperature, including the supercooled regime, are insignificant.[37,38] It turns out that each H bond acts independently of other hydrogen bonds, therefore the relaxation has to be a Poissonian process [Eq. (5)]. Indeed we find that, after the short transient time that manifests librations, the long time decay of $P(t)$ is always a monoexponential function, irrespective of different H bond definitions (Fig. 7). This result is in agreement with some previous findings,[32,35] but not with others.[33,34] On the physical basis, it is hard to understand what would make a function such as $P(t)$ nonexponential, as it describes a continuous elementary process of breaking a bond. The long time decay of $Q(t)$, on the other hand, cannot be exponential, as the diffusion process sets in immediately after the bond breaks. Unlike $P(t), Q(t)$ has a memory, as diffusion determines whether a specific pair of water molecules are still near neighbors. Two molecules can diffuse apart only after the hydrogen bond between them breaks, and a broken bond can reform if a molecule reverses its direction and diffuses back to its partner. This aspect of hydrogen bond dynamics clearly introduces a continuum of relaxation times. Figure 8 compares $k(t)$ and $Q(t)$ (for both HB definitions). A remarkable resemblance between the two functions is observed, in agreement with our old phenomenological picture of the coupled dynamics of translational diffusion with the elementary process of breaking and reforming an H bond,[27] outlined in Sec. II.

Our results show that the first passage time probability density of hydrogen bonds, $P(t)$, *is* a single exponential function. While a different dividing surface, i.e., different HB definition used in the simulation affects the absolute values of relaxation times, obtained from the slopes of semilog plots, Table I, Fig. 7, it does not affect the functional form of $P(t)$. Note, however, that the definition of $P(t)$ requires the

HB population operator, h, to equal unity if an H is *continuously* bonded to a particular O, according to distance and angle, or energy criteria. Thus, adding a *temporal* resolution, t_t, to such criteria of 0.1 ps,[10,11] 0.25 ps,[9] 0.4 ps,[8] for example, whereby the bonds that break and reform at times $t \leqslant t_t$ are treated as intact, makes the calculated probability densities nonexponential at long times,[33,57] because in this case a hybride of $P(t)$ and $Q(t)$ is determined.

The present analysis sheds light on predictions made often in the literature relating the power-law distribution of $P(t)$ to the liquid–liquid phase transition hypothesis and second critical point in water at low temperatures.[48] Note that at least at room *T*, most of the correlation functions such as $s(t)$ decays due to the fast vibrational motions. In less than 1 ps, $s(t)$ already decays by an order of magnitude. Therefore, to obtain good statistics for long time tails, one must collect data over hundreds of picoseconds (hundreds of nanoseconds at low *T*). Extension of the present analysis to lower *T*, including the supercooled water is in progress. It has already been established, however, that correlations between adjacent H bonds seem to be very weak also in supercooled water.[36,38] For molecular pairs sharing a common H bond we find that the probabilities of participating in additional bonds are well described as statistically uncorrelated events.[38] Our calculations show that even in supercooled regime a correlated fluctuation for bond breaking to happen is not required.[38] Both findings are shown[38] to be in agreement with computer simulation results of Matsumoto and Ohmine[36] and with experimental findings.[1,2,58,59] Therefore, we expect the same exponential relaxation of functions like $P(t)$ as we observe it at room temperature water.[60]

The identity in Eq. (26) conforms with our numerical results. Table I provides numerical values for different H bond times determined from different approaches. Differentiating between average HB *lifetime*, Eq. (18), and average HB *persistence time*, Eq. (20), is not a matter of semantics. Obviously, for the same reason that makes the decay of $c_c(t)$ slower compared to the decay of $s(t)$,$\langle \tau_{ex} \rangle$ are longer than $\langle \tau_{\mathrm{HB}}^{\mathrm{MFPT}} \rangle$, Table I. In the former case we average over all bonds that ever existed. In the latter case we average over bonds present at any given time. Note the difference: all bonds contribute with equal weight to the former average, but longer lived bonds make a bigger contribution to the latter average than shorter lived ones. In the former case, every bond makes equal contribution because every bond has only one birth. In the latter case, longer lived bonds make many contributions to the average, because they are more likely to be sampled.

The ‘‘continuous’’ HB correlation functions are ill-defined because they strongly depend on the presumed location of the barrier. HB lifetimes should not be extracted from continuous HB correlation function, $c_c(t)$, as their values heavily depend on bond definition, as well as on sampling frequency, ν.

While ‘‘intermittent’’ HB correlation functions are better defined in these respects, two important caveats should be mentioned regarding direct calculations of intermittent HB lifetimes. The first one concerns the numerical method used. Only a calculation from time correlation function leads to results that are asymptotically independent of the length of simulation and system size. Direct bond counting, on the other hand, imposes both lower and upper limits on simulation time. It has to be much longer than the HB lifetime, but still short enough to make random reforming of broken bonds improbable. Clearly, the second condition is related to the finite size of simulated system. The second caveat is the decay of the correlation function itself. $c(t)$ is nonexponential reflecting the fact that different dynamic processes contribute to the decay of this function.[27] Thus, one determines *correlation time*, not *relaxation time*. Only in the case of a single exponential relaxation these two times are equal. Clearly, one should not determine ‘‘intermittent’’ HB lifetimes from the zero frequency part of $c(t)$ (see Table I), or by assuming a quasiexponential decay of this function. Such determinations are arbitrary as the result depends on a specific interval over which these functions are studied.

Experimental determinations are always limited by a finite temporal resolution (experimental window in terms of energy resolution). Scattering techniques cannot assess small amplitude librations on a very fast time scale. They determine how long a proton stays in a cone (the range of librational angles corresponding to bond ON), before it leaves (corresponding to bond OFF). The latter event could coincide with libration movements that have large amplitude and may eventually bring the H atom sufficiently far from the O–O alignment between two neighboring molecules. In view of this picture,[1,2] a theorist would agree that a true HB lifetime in water, i.e., the time that represents the true breaking of a bond should leave out small amplitude librational motions on a very fast time scale in a sense introduced in the concept of ‘‘intermittent’’ HB lifetimes. So, in the parlance of Rapaport's work,[16] the alternative to ‘‘continuum at all times’’ or ‘‘intermittent at all times’’ should be intermittent on the time scale of librations, and continuous afterwards.

Calculating $P(t)$ with an arbitrary temporal definition of an H bond of several librational frequencies[11,33,57] is not the best solution for reasons already discussed: because of diffusion that happens on every time scale, including the time scale of bond breaking/reforming,[27] a bond can be broken for a time longer than the librational period and still has a greater than random probability of reforming. The resulting hybride of $P(t)$ and $Q(t)$ is nonexponential over all time scales.

For rigorous determinations of times that specify H bond dynamics, including the actual HB lifetimes, the reactive flux method offers a more powerful approach. It takes into account all the above-mentioned difficulties naturally. We calculate the time derivative of the intermittent HB correlation function, whose long time behavior, i.e., post-transient time is independent of the location of the dividing surface, and combine it with an appropriate phenomenology [Eq. (10)]. The macroscopic rate law is only expected to be applicable on a coarse grained time scale which does not resolve short time transient behavior. A *measured* correlation function will still, however, contain this short time information. By equating the reactive flux function with a phenomenological rate law [Eq. (10)], we disentangle the breaking and reforming dynamic elementary processes. Thus, we can extract from

TABLE II. Dependence of hydrogen bond (HB) times determined from different approaches [from (A) to (H), see Table I] on several of the conditions of concrete calculation. ‘‘no’’ denotes there is no dependence of calculated HB times on HB definition, sampling frequency, fitting interval, integration limits, time of simulation and size of the system (provided the length of simulation and system size suffice for good statistics).

HB times from Table I	HB definition	Sampling frequency, ν	Fitting interval	Integration limits	Time of simulation	Size of the system
(A)	yes	yes	N/A	no	no	no
(B)	yes	yes	N/A	N/A	no	no
(C)	yes	yes	N/A	N/A	no (if $\nu \ll \tau_{\mathrm{HB}}$)	no
(D)	yes	yes	N/A	no	no	no
(E)	yes	yes	N/A	N/A	no	no
(F)	(yes)	no	N/A	N/A	yes	yes
(G)	(yes)	no	no	yes	yes	yes
(H)	no	no	no	no	no	no

simulations the actual hydrogen bond lifetime, $\tau_{\mathrm{HB}}=1/k$, that is due solely to H bond dynamics of breaking. It does not include other dynamical processes that demonstrably happen on the same time scale, i.e., time for reforming an H bond, $1/k'$, time for its switching allegiance,[61,47] $1/(k+k')$, and diffusion time, τ_d.[27]

In the case of water, recrossings of the dividing surface turn out to be significant. For the optimized dividing surface, giving us the lowest value of k_{TST}, we observe that over the transient period of ~0.2 ps the reactive flux falls to ~30% of its initial value (Fig. 8, inset; Table I). The significant deviation of the actual reaction rate from the transition state theory estimate indicates that a large fraction of trajectories will recross the dividing surface before relaxing into a stable state, i.e., broken bond. Evidently, librational motions and inter-oxygen vibrations play a significant role in the H bond breaking dynamics. In the present system, $1/k(0^+)\equiv 1/k_{\mathrm{TST}}$ is about 70% smaller than the actual relaxation time, $1/k$, the time that captures very fast transient relaxation dynamics due to librations. While the first value obviously strongly depends on the hydrogen bonding criteria used in the simulation (inset of Fig. 8), the latter value is insensitive to such definition, (Fig. 8, solid curves). Note that our MD results, suggesting that ~70% of breaking bonds reform within the short transient time, compare well with the result of the dynamic path-sampling method, which does not rely on assumptions about the reaction coordinate.[62] Thus, our choice of dividing surface seems to be pretty close to the saddle point.

Table II shows that all the H bond times, except $1/k$, depend on several of the conditions of concrete calculation. Clearly, defining an H bond in a simulation includes an element of arbitrariness. However, the predictions of measurable properties (such as τ_{HB}, although indirectly) must be demonstrably independent of the criteria used to define reactants (bond ON), and products (bond OFF). Under conditions where barrier recrossings are frequent, such as is the case in liquid water, it is important to have an expression for the rate constant≡1/(average HB lifetime) that is independent of the precise location of the dividing surface (i.e., HB definition in the simulation). Reactive flux method combined with an appropriate phenomenology provides us with such an expression. Therefore, to construct yet another arbitrary workable definition of H bond for dynamical situations[63] seems unnecessary.

The absolute values presented in Table I are expected to change when using another potential model for water. For example, polarizable models for water permit longer intervals when a bond is absent than do nonpolarizable models.[10] Note that the emphasis of present calculations is not on absolute numbers, but rather on their trends and relative dynamics. In general, MD simulations with different potential models and methods obtain a variety of values at ambient conditions, which are of the *order of magnitude* of 1 ps. This value also coincides with indirect experimental determinations.[1,2] However, in other H bonded systems, in particular where we expect longer HB lifetimes and different mechanisms for H bond breaking,[64] quantitative differences between the different measures of relative dynamics become much more pronounced.[47] Therefore, it is important to keep in mind which calculated ‘‘HB lifetime’’ we should compare with experimental values, and which we should not.[65] Because of the finite resolution of observation times (finite temporal resolution) in experiments that indirectly determine HB lifetime in water, $1/k_{\mathrm{TST}}$ cannot be assessed. Thus, comparisons of relaxation times obtained from depolarized Rayleigh scattering[1] with simulation values determined from $1/\int_0^\infty tP(t)dt \equiv 1/\langle \tau_{\mathrm{HB}}^{\mathrm{MFPT}} \rangle$[34] cannot be conclusive. Transient vibrational spectroscopy shows that the excited H bond relaxes within a time constant of $1\pm 0.5\,\mathrm{ps}$.[4] This time should correspond to $1/k$. It should also correspond to the H bond relaxation time that is extracted from neutron scattering,[2] or depolarized Rayleigh scattering,[1] provided that the mechanism for H bond breaking primarily occurs through librational/vibrational motions (hindered rotations).[64] As $1/k$ describes an elementary process of breaking an H bond, it obviously gives an Arrhenius temperature dependence (not shown here), in agreement with experimental findings.[1,2,59]

V. CONCLUDING REMARKS

Central results of this paper are given by relations in Eqs. (32) and (26). The first one provides a different perspective on reactive flux HB correlation function, $k(t)$, by establishing its relation with first passage time probability densities for bonds that are created at $t=0$, $P(t)$, and for first reforming for bonds broken at $t=0$, $Q(t)$. The present analysis clearly shows that the probability density for hydrogen bonds, $P(t)$, is a single exponential function, and that $Q(t)$ is nonexponential for the same reason that makes $k(t)$ nonexponential, i.e., because of molecular diffusion. Thus, we demonstrate once again[27] that having a distribution of relaxation times in functions like $c(t)$ and $k(t)$ is a consequence of molecular diffusion. It is not a characteristics of an elementary H bond dynamic process in liquid water, which is described by well-defined rate constants for bond breaking and making.[27] However, these two dynamical process are coupled with diffusion. It has been shown that the simple diffusion model for H bond kinetics[27] (Sec. II), which accounts for this coupling successfully describes the time dependence of HB correlation functions obtained from simulations. A different approach has been recently applied to analyze the HB correlation functions such as $c(t)$ and $k(t)$.[34] This approach uses some concepts of mode coupling theory.[66] In view of the present work, and earlier analysis,[27] invoking such a sophisticated theory to interpret the time dependence of these functions seems not to be necessary.

As the average HB lifetime is often obtained from the mean of the distribution of HB lifetimes,[33–35] it is important to note two obvious implications that follow from the identity in Eq. (26): First, the TST rate constant is exact if there is no recrossing of the transition state barrier, i.e., transmission coefficient $\kappa=1$. As discussed in Sec. II, H bond kinetics in liquid water does not satisfy this condition. The plateau value of the transmission coefficient, $\kappa=k_{A\rightarrow B}/k_{\mathrm{TST}}$ provides us with the correction that has to be applied to the crossing rate predicted by TST. Therefore, $\langle\tau_{\mathrm{HB}}^{\mathrm{MFPT}}\rangle=\int_0^\infty tP(t)dt=1/k_{\mathrm{TST}}$ represents a *lower bound* to the actual HB lifetime, $\tau_{\mathrm{HB}}\equiv 1/k$. As we have seen, due to dynamical effects, TST underestimates HB lifetimes in water up to an order of magnitude. Obviously, its value has to be labeled with a particular HB definition used, and also depends on the sampling frequency (Table II). Second, the temperature dependence of average HB lifetimes obtained from $\int_0^\infty tP(t)dt$, Eq. (18), can only follow the Arrhenius law, as $k_{\mathrm{TST}}\propto\exp(-\Delta F^*/k_BT)$, where ΔF^* is the activation free energy. The above assertion is not compatible with power-law behavior of average H bond lifetime.[33] A possible reason that such power law has been observed[33] is the use of *temporal* H bond definition,[8] in addition to energetic/geometric criteria used, leading to a seemingly complicated picture of HB dynamics that in fact can rather be attributed to molecular motion, i.e., spatial diffusion.

Finally, we emphasize the obvious advantage of using reactive flux method in comparison with other conventional treatments of kinetic properties of hydrogen bonding liquids. This approach has been developed to study the dynamics of rare events in molecular liquids. Although making/breaking of H bonds in water is not a rare event,[67] the same methodology proves useful and advantageous to study kinetic properties over traditional methods which can provide us only with an off-hand estimate of relaxation times (Table II). The reactive flux, $k(t)$, which is always well defined in terms of molecular dynamics, gives information about transient relaxation, showing when most of the dynamics in the system is over. Therefore, there is no need to arbitrarily remove librations by invoking a temporal definition of a bond.[7–11] It gives us the TST approximation for the rate, and thus a lower bound to the average HB lifetime that other methods extract from lengthy calculations of $P(t)$.[34] And most importantly, combined with appropriate phenomenology, it provides a coherent picture of H bond relaxation kinetics, and actual HB lifetimes, $1/k$, all of which are independent of H bond definition in a simulation.

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