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Hydrogen-bond kinetics in liquid water

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HYDROGEN bonds play a crucial role in the behaviour of water^{1–4}; their spatial patterns and fluctuations characterize the structure and dynamics of the liquid^{5–7}. The processes of breaking and making hydrogen bonds in the condensed phase can be probed indirectly by a variety of experimental techniques⁸, and more quantitative information can be obtained from computer simulations⁹. In particular, simulations have revealed that on long timescales the relaxation behaviour of hydrogen bonds in liquid water exhibit non-exponential kinetics^{7,10–13}, suggesting that bond making and breaking are not simple processes characterized by well defined rate constants. Here we show that these kinetics can be understood in terms of an interplay between diffusion and hydrogen-bond dynamics. In our model, which can be extended to other hydrogen-bonded liquids, diffusion governs whether a specific pair of water molecules are near neighbours, and hydrogen bonds between such pairs form and persist at random with average lifetimes determined by rate constants for bond making and breaking.

In a computer model of liquid water, an instantaneous configuration, $r(t)$, denotes the positions of all the atoms in the system at time t . A configurational criterion for whether a particular pair of water molecules is bonded allows one to define a hydrogen-bond population operator, $h[r(t)] = h(t)$. This operator has a value 1 when the particular tagged pair, say molecules 1 and 2, are bonded, and zero otherwise. The average number of hydrogen bonds in an equilibrium fluid of N water molecules is $\frac{1}{2}N(N-1)\langle h \rangle$, where $\langle h \rangle$ denotes the average of $h[r(t)]$.

In the dynamic equilibrium of liquid water, hydrogen-bond populations fluctuate in time. The fluctuations are characterized by the correlation function

$$c(t) = \langle h(0)h(t) \rangle / \langle h \rangle \quad (1)$$

This function is the probability that the hydrogen bond is intact at time t , given that it was intact at time zero. It is computed from a simulation trajectory by recording the joint occurrences of two non-zero populations separated by a time t . At equilibrium, the probability that a specific pair is bonded in a large system is negligibly small. As a result, $c(t)$ relaxes to zero. According to the principles of statistical mechanics, specifically the fluctuation-

dissipation theorem¹⁴, this time evolution of $c(t)$ is the same as that for an initially prepared non-equilibrium concentration of hydrogen bonds. The rate of relaxation to equilibrium is

$$k(t) = -dc/dt = -\langle \dot{h}(0)[1 - h(t)] \rangle / \langle h \rangle \quad (2)$$

where $\dot{h}(0) = (dh/dt)_{t=0}$. Note that, because $\langle h(0)\dot{h}(t) \rangle = -\langle \dot{h}(0)h(t) \rangle$ and $\langle \dot{h}(0) \rangle = 0$, equation (2) follows from equation (1). Thus $-k(t)$ is the average rate of change of hydrogen-bond population for those trajectories where the bond is broken at a time t later. Figure 1 shows the $k(t)$ determined from our simulations of water at room temperature.

At short times, $k(t)$ manifests an assortment of motions leading to hydrogen-bond breaking. The most important of these motions are librations on the timescale of less than 0.1 ps, and inter-oxygen vibrations on the timescale of 0.1–0.2 ps. Beyond this transient period, $k(t)$ decays monotonically. To the extent that each hydrogen bond acts independently of other hydrogen bonds and also independently of other processes of similar timescales, the long time decay of $k(t)$ would be that of first-order kinetics^{15,16}. That is, one would expect $k(t) \approx v \exp(-vt)$, where $1/v$ would be the average hydrogen-bond lifetime. But as seen in Fig. 1, the post-transient relaxation of $k(t)$ is decidedly different. Beyond the transient, the slope of $\log k(t)$ increases monotonically with time t . The log-log plot shows clearly that this behaviour does not coincide with a power-law decay.

The distribution of hydrogen-bond lifetimes provides a complementary view of hydrogen-bond dynamics. This distribution is determined from trajectory calculations by recording the separate lengths of time over which $h[r(t)] = 1$. The functions $c(t)$ and $k(t)$ would decay exponentially if, and only if, the lifetime distribution were also exponential. The lifetime distribution is, however, non-exponential¹¹. Over a limited range of times, it exhibits power-law

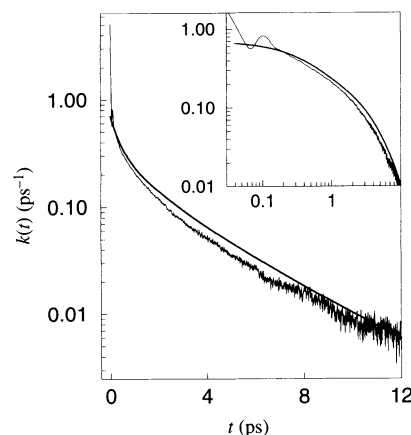


FIG. 1 The rate function, $k(t)$, computed from the trajectories of a molecular-dynamics computer simulation (thin line) and from the diffusion model (thick line). The simulation was for water at room temperature, and with a density of 1 g cm^{-3} . The length of the trajectory coincided with 240 ps of physical time. It employed the SPC potential model for water²³, using periodic boundary conditions and Ewald sums²⁴. In analysing the trajectory, two water molecules are considered to be hydrogen-bonded only if their inter-oxygen distance is $< 3.5 \text{ \AA}$, and simultaneously the angle between the O–O axis and one of the O–H bonds is 30° (ref. 19). There exists an assortment of reasonable alternative choices corresponding to different surfaces in configuration space dividing bonded from unbonded regions. Because trajectories flow quickly between nearby dividing surfaces, however, the behaviour of $k(t)$ is sensitive to hydrogen-bond definition for short times only. Beyond the transient period, the behavior of $k(t)$ is invariant to physically reasonable changes in hydrogen-bond definition. The main figure is a semi-log plot, the inset is a log-log plot. For the diffusion model, $k(t)$ is the inverse Laplace transform of $\bar{k}(s) = k/[s + k + k'sf(s)]$, where $f(s) = 3\tau[1 - \sqrt{s\tau} \arctan(1/\sqrt{s\tau})]$. These are the relationships obtained from the solution of equations (5) and (6) in the text. The inverse Laplace transform is evaluated by numerical integration. The parameters used in the plots are $\tau = 0.4 \text{ ps}$, $k = 0.7 \text{ ps}^{-1}$ and $k' = 1.0 \text{ ps}^{-1}$.

behaviour¹¹. These dynamic properties of a single tagged hydrogen bond should not be confused with that of the total population of hydrogen bonds. Because the total number of hydrogen bonds is extensive, their fluctuations are relatively small¹⁴, and the correlation function for the total number of hydrogen bonds appears exponential on the timescale of picoseconds (ref. 17).

It is unlikely that the source of non-exponential kinetics of tagged hydrogen bonds in water is due to correlations between different hydrogen bonds. The lifetime distribution that exhibits a power law for only a limited range of times suggests that correlations do not persist over large lengths and thus do not involve many hydrogen bonds. Further, the apparent exponential kinetics of the total hydrogen-bond population suggests that this collective variable is a sum of many statistically independent entities. Most importantly, however, by partitioning the trajectories that contribute to $k(t)$ according to the density of hydrogen bonds that are neighbours to a tagged bond, we have found that the dependence at room temperature is insignificant (A.L. and D.C., unpublished data).

A more likely source of significant non-exponential relaxation at ambient conditions is the coupling between hydrogen-bond population and diffusion. Two bonded molecules can diffuse apart only if the hydrogen bond between them breaks. Further, a broken hydrogen bond can reform if a molecule reverses its direction and diffuses back to its partner. To examine the quantitative consequences of diffusion, we have partitioned the contributions to $k(t)$ according to whether or not the pair has moved apart after its bond has broken. From this partitioning, we have computed

$$k_{in}(t) = -\langle \dot{h}(0)[1 - h(t)]H(t) \rangle / \langle h \rangle \quad (3)$$

Here $H(t)$ is unity if the oxygen–oxygen distance of the tagged pair is not larger than some distance $R = 3.5 \text{ \AA}$, and it is zero otherwise. In the hydrogen-bond definition we employ^{18,19}, two water molecules separated by less than 3.5 \AA can be either bonded or not bonded, depending upon their relative orientations. At larger separations, a bond cannot form. The first coordination shell of water, as measured by its oxygen–oxygen radial distribution function²⁰, extends to $\sim 3.5 \text{ \AA}$.

The probability at time t that a pair of initially bonded water molecules are now unbonded but remain separated by less than R is

$$n(t) = \int_0^t dt' k_{in}(t') \quad (4)$$

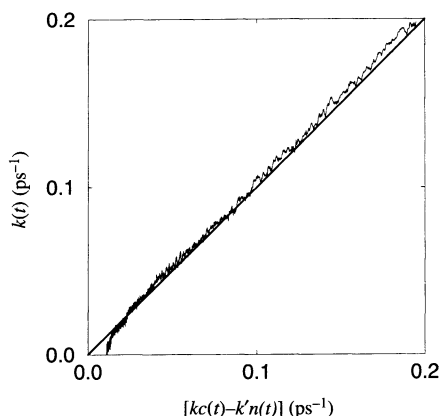


FIG. 2 Correlation plot relating the functions $c(t)$, $n(t)$ and $k(t)$ (see text), obtained from the molecular-dynamics computer simulation, for times t from 1 to 20 ps. At shorter times, deviations from the correlation are large. At longer times, statistical uncertainties of the simulation results preclude a test of the correlation. The validity of equation (5) is judged by comparing the simulation data (jagged line) with the straight line of unit slope. A description of the simulation is given in Fig. 1 legend. The values of the constants k and k' used in the plot are 0.7 ps^{-1} and 1.0 ps^{-1} , respectively.

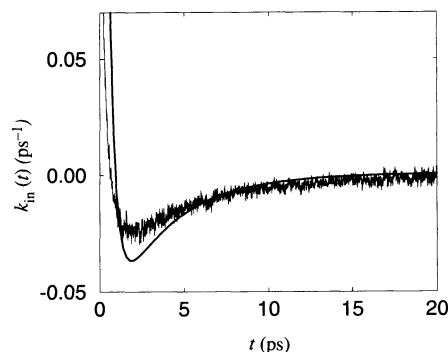


FIG. 3 The restricted rate function, $k_{in}(t)$, as computed from trajectories of a molecular-dynamics simulation (thin line) and from the diffusion model (thick line). A description of the computer simulation is given in Fig. 1 legend. For the diffusion model, $k_{in}(t)$ is the inverse Laplace transform of $\tilde{k}_{in}(s) = s\tilde{f}(s)\tilde{k}(s)$, where $\tilde{k}(s)$ and $\tilde{f}(s)$ are given in the Fig. 1 legend. The inverse Laplace transform is evaluated by numerical integration. The parameters used in the plot are $\tau = 0.4 \text{ ps}$, $k = 0.7 \text{ ps}^{-1}$ and $k' = 1.0 \text{ ps}^{-1}$.

The probabilities $c(t)$ and $n(t)$ correspond to local populations that can interconvert. Hence, their kinetics might follow

$$dc/dt = -kc(t) + k'n(t) \quad (5)$$

where k and k' (not to be confused with the function $k(t)$) are the respective rate constants for the breaking and making of hydrogen bonds between a near-neighbour pair of water molecules. The correlation plot given in Fig. 2 shows that with $k = 0.7 \text{ ps}^{-1}$ and $k' = 1.0 \text{ ps}^{-1}$ equation (5) is consistent with the results of our computer simulation for times beyond the transient period. If k and k' differ by more than 10% from these values, the simulation data deviate significantly from the line of unit slope. The relaxation rate constants thus identified for hydrogen bonds in water are material properties. For example, the values of k and k' depend on the temperature and concentration of solutes in the system, and will also be sensitive to H/D isotopic variation. Similarly, for simulations, the values of k and k' can depend on the model used. Irrespective of the system, however, equation (5) provides the connection between rigorous microscopic dynamics and hydrogen-bond rate constants.

The physical meaning of $1/k$ is that of the average hydrogen-bond lifetime. The value obtained from the correlation plot is 1.4 ps. Essentially the same average lifetime is obtained from the distribution of lifetimes in our simulation, as should be the case if equation (5) is correct. In the broken bond state, the bond between the tagged pair of molecules, 1 and 2, no longer exists as these molecules are now bonded to other nearby partners. The average frequency of switching allegiances is $k + k'$, which is 1.7 ps^{-1} in the simulation model.

To the extent that $n(t)$ is non-zero, the two tagged molecules are no longer bonded to each other but remain within a distance R . The population $n(t)$ is therefore a measure of local strain in the hydrogen bonds. It will relax not only by conversion back to the bonded state, but also by diffusion. If this diffusion were to occur slowly enough, $c(t) + n(t)$ would appear to be a constant. The separate populations, $c(t)$ and $n(t)$, would each change by interconversion only, relaxing as single exponentials. But diffusion can occur on a time scale that is comparable to $1/k$ and $1/k'$.

The degree to which diffusion is significant can be estimated from

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) = D \nabla^2 \rho(\mathbf{r}, t) + \delta(\mathbf{r}) [kc(t) - k'n(t)] \quad (6)$$

Here $\rho(\mathbf{r}, t)$ represents the density of the diffusing unbonded pair, where \mathbf{r} is the vector between the pair, and D is the interdiffusion constant for the pair. Equation (6) is restricted to timescales larger than that of the transient interval, and to length scales larger than the spatial width of a hydrogen bond. Greater resolution would

require changing k , k' and D from constants to operators that are non-local in space and time. The delta function of the source and sink terms in equation (6) localizes \mathbf{r} to within a volume a^3 , where a is the range of lengths over which a hydrogen bond might exist. The quantity $\rho(\mathbf{0}, t)$ is thus $n(t)/a^3$. This connection, with equations (5) and (6) gives three equations for three unknowns, and these comprise a diffusion model for hydrogen-bond kinetics. The model can be solved straightforwardly for $k(t)$ and $k_{in}(t)$. The solution depends on the length a as it appears in the time $\tau = a^2/D(6\pi^2)^{2/3}$. Diffusion constants of water are of the order of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The radius of a water molecule is $\sim 1.5 \text{ \AA}$. Thus, τ is expected to be in the range of 0.1–1 ps, neither short nor long compared to $1/k$ and $1/k'$.

Figure 1 shows a comparison of $k(t)$ obtained from our computer simulation with that obtained from the diffusion model with $\tau = 0.4 \text{ ps}$ and with k and k' fixed at the values found from the correlation plot, Fig. 2. Less favourable comparisons are found by varying τ by 25% from this value. A similar comparison using the same values of k , k' and τ is made in Fig. 3 for $k_{in}(t)$. The diffusion model is seen to provide an explanation of most of what is found from the computer simulation calculations, including the fact that $k_{in}(t)$ becomes negative after a period of somewhat less than 1 ps. This behaviour is associated with trajectories that initially have a $\dot{h}(0) > 0$, and thus initially enter into a hydrogen bond. These trajectories are trapped, re-emerging only later into the unbonded region of configuration space.

Quantitative improvements to the diffusion model could be made by refining its resolution in space and time. Independent of such improvements, our analysis establishes the existence of well defined rate constants k and k' and their connection to microscopic correlation functions. This connection can be used in general to analyse the dynamics of hydrogen-bonded liquids. Our phenomenological model can be applied to interpret inco-

herent neutron scattering²¹ and perhaps transient vibrational spectroscopy²². Experimental verification of the model will require coordinated application of two different techniques because $c(t)$ and $n(t)$ are independent functions that vary on the same timescale. □

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Dynamics of CO₂-driven lake eruptions

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ON 21 August 1986, a massive release of carbon dioxide from Lake Nyos in Cameroon killed about 1,700 people. A similar event occurred on 15 August 1984 at Lake Monoun, also in Cameroon. It was suggested^{1–5} that the CO₂ released was initially dissolved in the hypolimnion (dense lower layer) of the lake, and was released by eruptive outgassing. Because of its violence, the Nyos outburst was at first thought⁶ to have been volcanic, but undisturbed sediments and other evidence indicate that no large volcanic eruption occurred^{7–9}. Recent experiments^{10,11} have shown that decompression of CO₂-saturated water is able to power explosive eruptions. Here I analyse the dynamics of CO₂-driven lake-water eruptions by deriving an equation of state for gas–liquid mixtures and using it to integrate the Bernoulli equation, which describes the dynamics of the bubbly flow. I find that under certain conditions these eruptions can be violent: the lake-surface exit velocity of an initially gas-saturated water parcel may reach 89 m s^{-1} for Lake Nyos and 51 m s^{-1} for Lake Monoun. The dynamics are similar to those of water-driven volcanic eruptions, which are also powered by gas exsolution from a liquid.

The dissolved CO₂ content of the water of Lake Nyos, and hence the density of that water, increases with depth owing to slow leakage of magmatic CO₂ into the lake^{8,9}. But as the partial pressure of CO₂ (p_{CO_2}) in the water increases, the hydrostatically

stable water at the lake bottom becomes increasingly dynamically unstable because a small perturbation due to a landslide, sinking of cold rain water, an internal wave, a small volcanic injection of CO₂, or a heavy flood of water into the lake might move the water up sufficiently to reach saturation ($p_{\text{CO}_2} = P_{\text{total}}$), allowing bubbles to form and grow. Being less dense than the surrounding water, the bubbly water ascends with increasing speed, resulting in an “overturn” of the lake or a limnic eruption¹, which releases the lethal CO₂ (ref. 9). The dynamics of CO₂-driven limnic eruptions have not been fully investigated¹².

Rise of CO₂-saturated water may be explosive because of strong positive feedback between bubble formation and growth, volume expansion and buoyancy rise. Once triggered, uprising of bottom water may form an erupting “conduit”^{13,14} into which more bottom water may be drawn (Fig. 1), allowing it to sustain itself throughout the eruption. In the Lake Nyos eruption, an estimated $(1–3) \times 10^8 \text{ kg}$ of CO₂ (refs 5, 9) was released during an eruption that possibly lasted as long as 4.5 hours (ref. 12). Hence the process probably lasted much longer than the time needed for a water parcel to ascend through the erupting conduit ($\leq 10 \text{ s}$, see later discussion on ascent velocity). That is, the process may be roughly at steady-state. Steady state also requires that the pressure in the conduit at each depth be independent of time. Because the medium through which limnic eruptions occur is fluid, the pressure P at each depth in the erupting conduit is roughly hydrostatic (denoted as P_h) and hence independent of time. Otherwise, water surrounding the conduit would flow into, compress and constrict the conduit so as to maintain hydrostatic equilibrium if the pressure in the conduit at each depth is less than P_h ; surrounding water would flow away to let the conduit expand if the pressure inside the conduit is greater than P_h . The approximate independence of pressure with time shows that the