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Correlations among Hydrogen Bonds in Liquid Water

Paolo Raiteri*
INFM, UdR Milano-Bicocca, Via Cozzi 53, I-20126 Milano, Italy

Alessandro Laio
Computational Science, Department of Chemistry and Applied Biosciences, ETH Zurich, c/o USI Campus,
Via Buffi 13, CH-6900 Lugano, Switzerland

Michele Parrinello
Computational Science, Department of Chemistry and Applied Biosciences, ETH Zurich, c/o USI Campus,
Via Buffi 13, CH-6900 Lugano, Switzerland

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By performing computer simulations of water with the TIP5P potential we show that structures formed by two or more hydrogen bonds affect the dynamical and static properties of water, especially in the vicinity of freezing temperature. In particular, the short time correlation between two coupled hydrogen bonds cannot be predicted assuming the statistical independence of the single hydrogen bonds. This introduces an additional relaxation time of ~9 ps close to the freezing point. We also find that the time persistence of structures formed by several hydrogen bonds (the first solvation shell) correlates with the local density, which is smaller around water molecules with a long-living environment.

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In simple liquids local structures involving three or more molecules have a very short lifetime. However, hydrogen-bonded substances, such as water, are far from being simple liquids [1,2]. In liquid water, each molecule forms on average ~4 hydrogen bonds (HBs) giving rise to a continuous random network [3,4], and it has long been debated whether or not supermolecular structures exist, especially close to the freezing point [5–7]. It has also been speculated that correlations among different HBs could play a role in determining the anomalous properties of water [8–10], such as the fact that ice can float, at variance with most other substances in which the solid is denser than the liquid. Luzar and Chandler studied the *single* HB dynamics by computer simulations [6,11] and concluded that the HB relaxation time does not depend on the local environment in the initial configuration. They deduced from this that many-body correlations in liquid water are of little importance [11]. On the other hand, Errington and Debenedetti pointed out that any anomalous behavior of liquid water is strictly connected to the density behavior and that molecules with a solid-like first solvation shell belong to clusters of up to 80 molecules [9,10]. The two pictures are not consistent, and it is therefore essential to obtain better insight into the intermolecular correlations and cooperative processes involving *more than one* hydrogen bond. The opportunity of using a very reliable intermolecular potential (TIP5P [12]) opens new possibilities for obtaining a molecular interpretation of the fundamental properties of water. In this Letter we provide a quantitative estimate of the stability of structures formed by more than one HB. We show that structures involving three or more molecules have lifetimes which are long on the atomic scale, increase with decreasing temperature, and nearly diverge below the freezing temperature. We also elucidate the connection between the local/structural properties and the persistence time of these structures formed by more than two water molecules, showing that the water anomalies can possibly be related to the existence of supermolecular structures.

We used the GROMACS code [13] to simulate 512 water molecules at different temperatures between 248 and 348 K, employing the TIP5P [12] potential. This model combines computational efficiency with good accuracy in describing the properties of water close to the freezing point. The self-diffusion coefficient and the density anomaly are indeed well reproduced by this potential [12,14,15]. The long-range interactions were computed with the particle mesh Ewald algorithm [16], which allows better energy conservation for long runs, and bond constraints are applied by the SHAKE algorithm [17]. The density of the system is fixed at the equilibrium value for the TIP5P potential at the corresponding temperatures [14]. Note that using the Ewald summation algorithm the density vs temperature curve is shifted and the temperature of maximum density is moved to 284 K [14]. We equilibrate the system for 0.5 ns with the Berendsen *et al.* thermostat [18], and then we perform a 1 ns run in the microcanonical ensemble at each temperature. The atomic coordinates are saved and analyzed every 0.1 ps.

Consistently with other approaches (see, e.g., Refs. [5,6]), we characterize the HB by a function of the atomic coordinates, h_{ij}, which can be either 1 or 0 depend-

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ing on whether or not an HB is formed between molecules i and j. In order to define h_{ij} we consider two smoothly decaying functions [19]. The first is a function of the $\overline{O_iO_j}$ distance, and it is one at 2.75 Å and decays to 0 at 3.50 Å, corresponding to the maximum and first minimum in the oxygen pair distribution function. The second is 1 when the sum of the $\overline{O_iH}$ and $\overline{HO_j}$ distances is equal to the $\overline{O_iO_j}$ distance and decays to zero when the difference exceeds 0.5 Å (H can belong to either molecule i or j). If the product of those two functions is greater than a threshold value of 0.5 $h_{ij} = 1$ and it is zero otherwise. We can easily distinguish between a formed or broken HB because the product of the two analytical functions is mainly close to 0 or to 1. Moreover, by changing the threshold between 0.2 and 0.8 the number of HBs in the samples is almost constant. Such a definition is qualitatively equivalent to more standard ones involving the angle between the O_iO_j and O_iH bonds [20] or the interaction energy between the molecules [21]. According to our definition, the average number of HBs formed by each molecule, $\langle n\rangle$, varies from 3.8 at 264 to 3.3 at 348 K. It is important to stress that the behavior of the time correlation functions (for a time longer than 1 ps) is not affected by the exact definition of h_{ij}, as already shown elsewhere [22].

In liquid water HBs evolve dynamically in time and, given a sample of N water molecules, we define the following correlation functions describing the time behavior of a single HB, $c_{w_1}(t)$, of two neighboring HBs, $c_{w_2}(t)$, and of the number of HBs formed by each molecule, $c_n(t)$:

$$c_{w_1}(t) = \frac{1}{N}\sum_{i\neq j}\langle \tilde{h}_{ij}(t_0)\tilde{h}_{ij}(t_0+t)\rangle, \tag{1}$$

$$c_{w_2}(t) = \frac{1}{N}\sum_{\substack{i\neq j\\ k\neq j,i}}\langle \tilde{h}_{ij}(t_0)\tilde{h}_{jk}(t_0)\tilde{h}_{ij}(t_0+t)\tilde{h}_{jk}(t_0+t)\rangle, \tag{2}$$

$$c_n(t) = \frac{1}{N}\sum_{i}\langle n_i(t_0)n_i(t_0+t)\rangle, \tag{3}$$

where $\tilde{h}_{ij} = h_{ij} - \langle n\rangle/N$, $n_i(t) = \sum_j h_{ij}(t)$ is the number of HBs formed by the ith molecule and $\langle\,\rangle$ indicates an average over t_0. Note that in Eqs. (1) and (2) the trivial correlation due to the finite size of our system $\langle n\rangle/N$ has been subtracted from the HB operator h_{ij}. According to these definitions $c_{w_1}(0) = \langle n\rangle + O(1/N)$, $c_{w_1}(\infty) = 0$, $c_{w_2}(0) = \langle n^2\rangle - \langle n\rangle + O(1/N)$, $c_{w_2}(\infty) = 0$, $c_n(0) = \langle n^2\rangle$, and $c_n(\infty) = \langle n\rangle^2$. A quantitative estimate of the lifetime of a given correlation function can be obtained by the relaxation time

$$\tau_\alpha = \frac{\int dt\, t c_\alpha(t)}{\int dt c_\alpha(t)} \tag{4}$$

with $\alpha = w_1$, w_2, and n. If the temperature is decreased, the relaxation time of a single HB (τ_{w_1}) grows abruptly before the freezing temperature of the model is reached (271 K [23]), close to the temperature of maximum density (284 K [14]), (Fig. 1, top panel). This behavior has already been reported by Starr *et al.* [7,22]. The numerical difference between our values of τ_{w_1} and those of Starr *et al.* can be traced back to the use of a different intermolecular potential and to slightly different thermodynamic conditions. The relaxation time of $c_{w_2}(t)$, and $c_n(t)$ displays the same behavior. The inset in the top panel of Fig. 1 shows that the temperature dependence of all the τ_α's cannot be fitted by a single exponential of the inverse temperature [6,7].

From Fig. 2(a) it can be seen that, for large t, $c_{w_2}(t) \sim [c_{w_1}(t)]^2$. This clearly indicates that, at long times, the

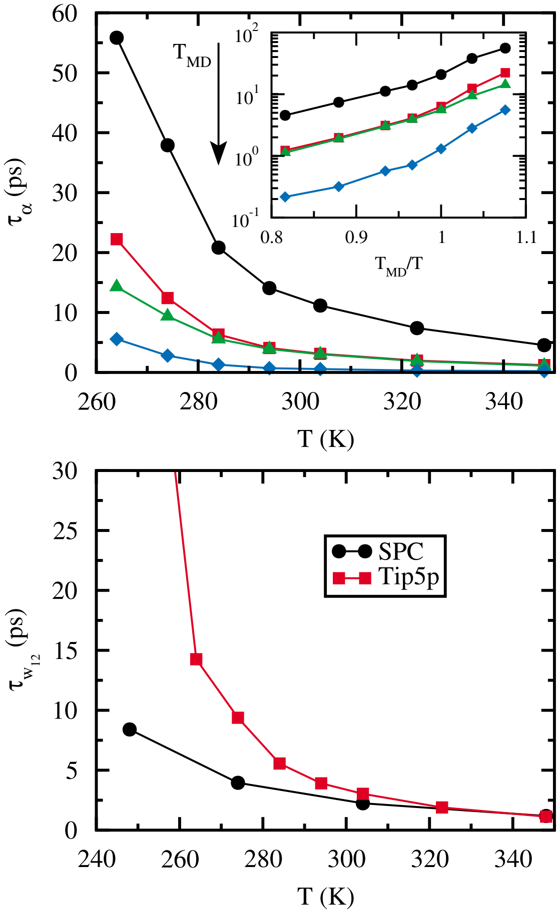

FIG. 1 (color). Top panel: lifetime τ_α (see text) of a single HB ($\alpha = w_1$, black circles) of two neighboring HBs ($\alpha = w_2$, red squares), of the HB-HB correlation ($\alpha = w_{12}$, green triangles), and of the number of HBs formed by each molecule ($\alpha = n$, blue diamonds). $T_{\rm MD}$ indicates the temperature of maximum density of the TIP5P model (284 K [14]). The inset is a semilogarithmic plot of τ_α's as a function of the inverse temperature. Bottom panel: comparison between $\tau_{w_{12}}$ as computed with the SPC potential and the TIP5P potential. Within our limited simulation time we can provide only a rough estimate of the value of $\tau_{w_{12}}$ for the TIP5P potential at 248 K (100 ps), and that is the reason why it is not explicitly shown in the picture.

two HBs behave independently from each other, in agreement with the analysis of Refs. [6,11]. However, a very clear fingerprint of correlation between different HBs shows up when we compare the short time behavior of $c_{w_2}(t)$ and $[c_{w_1}(t)]^2$, i.e., the time correlation function of two neighboring HBs and that of two statistically independent HBs. For $t = 0$ the difference between the two correlations is equal to $\langle n^2\rangle - \langle n\rangle^2 - \langle n\rangle + O(1/N)$, and this difference depends very weakly on the temperature. Moreover, it is similar for simple point charge (SPC) and TIP5P water (at 300 K, 2.82 and 2.75, respectively; for TIP5P ice Ih close to melting it is 3.80). Cooperative processes between neighboring HBs play a role in the short time regime and the combined correlation $c_{w_{12}}(t) = [c_{w_1}(t)]^2 - c_{w_2}(t)$ provides a quantitative measure of their importance. While at high temperature $c_{w_{12}}(t)$ survives only for a rather short time ($\tau_{w_{12}} \sim 1$ ps at 348 K), indicating an almost uncorrelated behavior, as the temperature is decreased $\tau_{w_{12}}$ grows abruptly: $\tau_{w_{12}} \sim 14$ ps for a sample at 264 K, and for $T = 248$ K $\tau_{w_{12}}$ becomes so large that, within our limited simulation time, we can provide only a rough estimate of 100 ps. Calculations with the SPC potential [21] reveal a much smoother temperature dependence: while at 348 K $\tau_{w_{12}}$ is very close to the TIP5P value, at lower temperature the SPC potential does not produce the almost diverging behavior for $\tau_{w_{12}}$ observed in TIP5P [Fig. 1 (bottom panel)]. This is not surprising, since the SPC potential predicts the water self-diffusion coefficient to be more than 1.5 times larger than the experimental value [15] and does not account for the density anomaly nor for the freezing. Thus, a trajectory obtained by the SPC potential represents a water effectively warmer than the simulation temperature and does not keep account of the importance of correlations between HBs [6,11]. On the other hand, the TIP5P potential (or the SPC/E potential [24] employed elsewhere for similar calculations [7,9,10]) provides a better description of the diffusive properties of water at the freezing point [15], and the capability of the model potential to account for the anomalous behavior of water is essential in order to describe correctly the physics of the system.

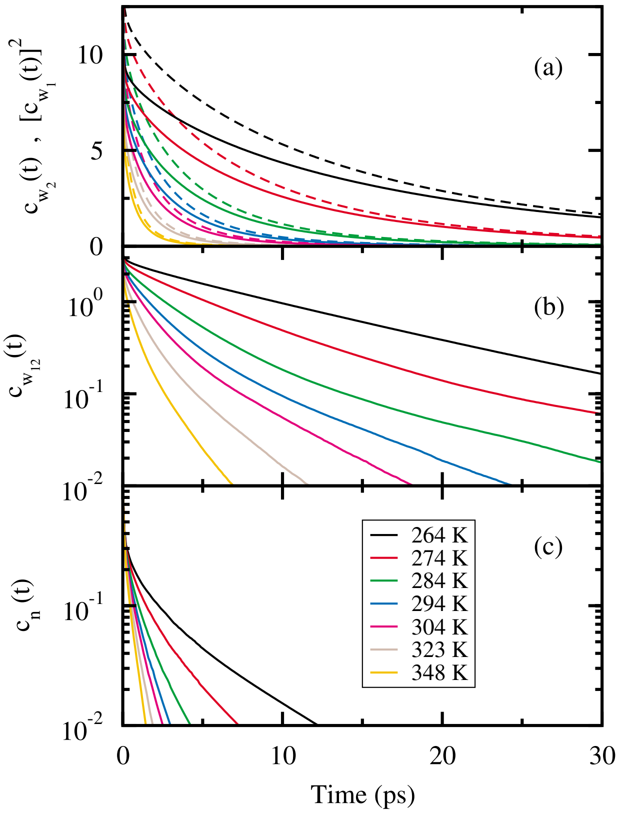

FIG. 2 (color). Time correlation function of two neighboring HBs, $c_{w_2}(t)$ [(a), solid lines], and of two statistically independent HBs, $[c_{w_1}(t)]^2$ [(a), dashed lines] and their difference, $c_{w_{12}}(t) = [c_{w_1}(t)]^2 - c_{w_2}(t)$ (b), computed from the atomic trajectories. In (c) the time correlation function of the number of HBs formed by each water molecule $c_n(t)$ is shown.

Correlations between different HBs become increasingly important as the temperature is decreased and should be accounted for in order to understand the properties of the liquid close to the freezing point. As a second example of this, we find an important correlation between the local density and the stability of the environment around each water molecule: in particular, we show that water molecules forming more stable structures with their neighbors belong to locally less dense regions.

The local density around the molecule i at time t can be estimated from the running coordination number $N_{i,t}(r)$,

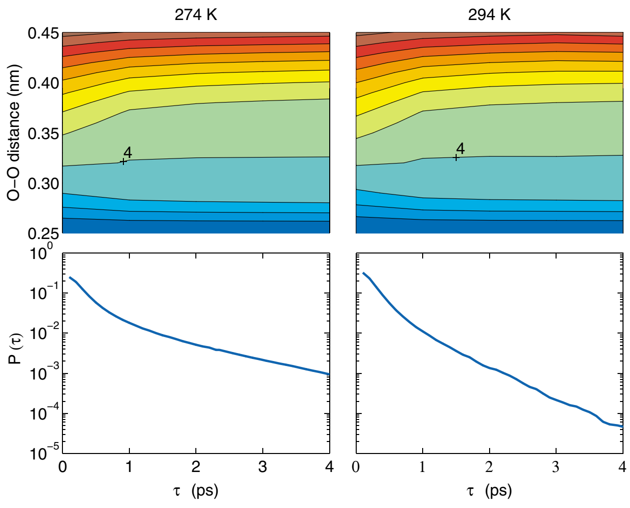

FIG. 3 (color). Top panels: contour plot of the running coordination number as a function of the persistence time [$\overline{N}(r, \tau)$; see the text] of the first solvation shell, for two selected temperatures: $T = 274$ and 294 K. The black lines represent where an integer number of neighbors is reached. A coordination number equal to 4 (labeled) corresponds to the first solvation shell. Analogous behavior is found for all the other temperatures analyzed (248–348 K). Bottom panels: normalized probability distribution of the water molecules with respect to τ, $P(\tau)$.

i.e., the number of molecules within a distance r from the molecule i. In order to quantify the stability of the local environment for each water molecule i, we compute the number of HBs as a function of time, $n_i(t)$, and we divide its trajectory into segments labeled by α of length τ_i^α during which $n_i(t)$ is constant. A large τ_i^α corresponds to a stable first solvation shell of the molecule i, since in that time interval $n_i(t)$ is constant and none of the HBs formed by molecule i is broken or exchanged. The correlation between τ and $N_{i,t}(r)$ is estimated by computing the two-dimensional histogram

$$\overline{N}(r,\tau) = \frac{\sum_{i,\alpha} \delta_{\tau_i^\alpha,\tau} \int_{\tau_i^\alpha} dt N_{i,t}(r)}{\sum_{i,\alpha} \delta_{\tau_i^\alpha,\tau} \tau_i^\alpha}, \qquad (5)$$

which represents, for every τ, the running coordination number averaged over all the molecules whose persistence time of the local environment is τ.

In Fig. 3 we show the contour plot of $\overline{N}(r,\tau)$ for two selected temperatures, each black line indicating where an integer number of neighbors is reached. The distance at which the first solvation shell is completed (labeled 4 in Fig. 3) increases with τ from 3.2 to 3.3 Å, showing that molecules belonging to a long-living configuration have, on average, a less dense environment (approximately 9%). The dependence on τ is very similar at all the temperatures we considered (248–348 K), while the number of water molecules whose environment survives for a time τ is a sharp function of the temperature: at low temperature a large fraction of molecules live in a stable environment, but the reverse occurs at higher temperatures (see Fig. 3, bottom panels). Hence, at low temperature, the fraction of molecules with a stable first solvation shell increases, leading to an average reduction of the density, which is in agreement with the experimental observation of the anomalous behavior of the water density.

Experimental investigation of the presence and importance of correlations between HBs in water would be very valuable, and a natural candidate to probe our theory is nonlinear infrared spectroscopy [25,26]. We suggest in this respect that coupling into the HOH bending modes might be particularly profitable, since this is modified by the presence of two neighboring HBs and therefore is sensitive to the many-body correlations described here.

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*Present address: Computational Science, Department of Chemistry and Applied Biosciences, ETH Zurich, c/o USI Campus, Via Buffi 13, CH-6900 Lugano, Switzerland.
Electronic address: praiteri@phys.chem.ethz.ch

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$$f(d) = \frac{1 - [(d - d_0)/\Delta]^n}{1 - [(d - d_0)/\Delta]^m},$$

where $d_0 = 2.75$, $\Delta = 0.45$, $n = 10$, and $m = 16$ if d is the $\overline{O_iO_j}$ distance or $d_0 = 0$, $\Delta = 0.4$, $n = 4$, and $m = 8$ if d is $\overline{O_iH} + \overline{O_jH} - \overline{O_iO_j}$.
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