

Fast Anomalous Diffusion of Small Hydrophobic Species in Water

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Using Car-Parrinello molecular dynamics a *structural* diffusion mechanism for the simplest hydrophobic species in water, an H atom, is proposed. The hydrophobic solvation cavity is a highly dynamical aggregate that actually *drives*, by its own hydrogen-bond fluctuations, the diffusion of the enclosed solute. This makes possible an anomalously fast diffusion that falls only short of that of “Grotthuss structural diffusion” of H^+ in water. Here, the picture of a *static*, i.e., “iceberglike,” clathrate cage is a misleading concept. The uncovered scenario is similar to the “dynamical hole mechanism” found in a very different context, that is, large molecules moving in hot polymeric melts.

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Hydrophobicity is at the root of many important phenomena, such as clathrate formation, preferential solvation, and protein folding. Thus, the properties of “hydrophobic species” in water are of considerable interest in physics, chemistry, and the life sciences as evidenced by many reviews [1–4] and a wealth of case studies [5–19]. What caught our particular interest some time ago was the observation that an H atom in ambient water, the simplest conceivable hydrophobic solute, diffuses only slightly “slower” than the famous proton H^+ in water (i.e., $D_H^{\text{exp}} \approx 7.0 \times 10^{-9} \text{ m}^2/\text{s}$ [20] vs $D_{H^+}^{\text{exp}} \approx 9.3 \times 10^{-9} \text{ m}^2/\text{s}$ [21]). In the latter case the anomalously fast diffusion — note that the self-diffusion coefficient is $D_{H_2O}^{\text{exp}} \approx 2.3 \times 10^{-9} \text{ m}^2/\text{s}$ [22] for ambient water — is possible only due to the so-called “structural” or “Grotthuss diffusion” mechanism; see Ref. [23] and references therein. Interestingly not only the H atom, but also other small hydrophobic solutes such as Mu, D, H_2 , He, or Ne show diffusion coefficients that exceed that of water by a factor of 2 to 6 [20], the Ne atom being heavier than an H_2O molecule. Despite this puzzling anomaly, the detailed *atomistic* mechanism underlying this phenomenon remained unexplained.

Along these lines a single H atom (labeled H^*) in water was investigated in a pioneering force-field molecular dynamics (MD) study nearly 20 years ago [8]. It was shown to create a bubble or cavity within the hydrogen-bonded network rather than being located interstitially. However, the authors stated clearly that “... it remains to not only justify our empirical potential functions but also to explore the role played by quantum effects...” One year later, the latter were shown to be negligible [9], whereas it was found out 10 years later that two reasonable potentials yielded dramatically *different* solvation [12]. A potential that was *fitted* to reproduce experimental data on H diffusion in ice led to peak maxima of g_{H^*O} and g_{H^*H} at 3.0 Å and 2.9 Å, respectively. This is *considerably* smaller than found previously [8] (3.8 Å and 3.5 Å, respectively) and will certainly impact both the structure and dynamics of the solvation shell.

Here, we resolve these issues using Car-Parrinello *ab initio* MD simulations [24,25]; for such recent studies of ions in water, see, e.g., Refs. [26–30]. In order to avoid unnecessary confusion we stress that the chemistry of the solvated hydrogen atom is totally different from that of the solvated hydrogen cation, i.e., the proton in water. The former is an essentially inert impurity sitting in a solvent cavity [8], whereas the latter immediately “reacts” with the solvent to form transient solvation complexes which are at the root of the Grotthuss mechanism [23]. Thus, despite the *phenomenological* similarity as to the anomalously fast diffusion, the underlying *mechanism* of the H atom and H^+ cation migration must be fundamentally different.

In our calculations one hydrogen atom H^* was surrounded by 63 H_2O molecules in a periodic 12.4 Å cubic box. Spin-polarized (i.e., unrestricted) BLYP (Becke-Lee-Yang-Parr) Car-Parrinello simulations of this open-shell (doublet) system were carried out [24,25,31]. The valence orbitals were expanded in plane waves up to a cutoff of 70 Ry at the Γ point in conjunction with Troullier-Martins pseudopotentials for the cores. After careful equilibration, 4.53 ps of trajectory were analyzed; as usual the deuterium mass was used for all hydrogens to allow for a time step of 8 a.u. The average temperature was 315 K as established by very gentle Nosé-Hoover thermostatting.

As a first step, the structure of the hydration shell of H^* is analyzed in Fig. 1. In agreement with general hydrophobic solvation concepts, the water molecules are arranged in the so-called “straddling orientation” [5,14] such that the hydrogens come somewhat closer to H^* than the oxygens. In particular, g_{H^*O} and g_{H^*H} peak around 3.0 Å and 2.9 Å, respectively, which is identical to the positions obtained from a potential that was actually *fitted* to H atom diffusion [12]. Thus, the average distance of H^* from the surrounding water molecules is similar to the O-O distance in the bulk (g_{OO} peaks around 2.8 Å in pure “BLYP water” at the same conditions [32]). The coordination number of H^* obtained from the first

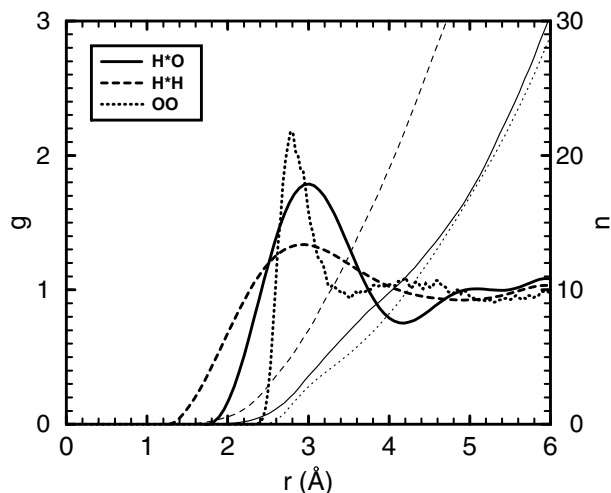


FIG. 1. Radial distribution functions g_{H^*O} (solid line), g_{H^*H} (dashed line), and g_{OO} (dotted line) and running coordination numbers n_{XY} (corresponding light lines) for one hydrogen atom H^* in liquid water at 315 K.

minima g_{H^*O} and g_{H^*H} is about 11 and 34, respectively; i.e., the solvation shell is considerably smaller than previously believed [8].

Additional insights into this can be gained from a topological analysis of the electronic structure using the electron localization function (ELF) [33]

$$\eta = \left[1 + \left(\frac{\frac{1}{2} \sum_i^{\text{occ}} |\nabla \psi_i|^2 - \frac{1}{8} \left(\frac{(\nabla \rho_\alpha)^2}{\rho_\alpha} + \frac{(\nabla \rho_\beta)^2}{\rho_\beta} \right)}{2^{2/3} C_F (\rho_\alpha^{5/3} + \rho_\beta^{5/3})} \right)^2 \right]^{-1}$$

in an open-shell spin-polarized formulation [34], where $\psi_i(\mathbf{r})$ and ρ_x denote orbitals and spin densities and $C_F = 3(3\pi^2)^{2/3}/10$. As already outlined in detail [33,34] $\eta(\mathbf{r})$ becomes large in those regions of space where two electrons with antiparallel spin are paired (forming covalent bonds or lone pairs) and/or where an *unpaired* electron tends to be well separated from all others. In addition to the covalent OH bonds (spherical localization domains) and the (peanut-shaped) lone pairs leading to hydrogen bonding, the special H atom, H^* , is clearly distinguishable in Fig. 2 with the by far largest domain. Further analysis shows that this domain stems largely from an unpaired electron as expected for an H atom, which stays like that during the entire simulation; see Fig. 3. More importantly, the shape of its localization domain is quite isotropic if the H atom is centered in cavity, see Fig. 2 (left panel), whereas the anisotropy in Fig. 2 (right panel) visualizes polarization of H^* by its hydration shell and thus deviations from a spherical wave function. This effect was not accounted for in previous force-field MD studies [8,9,12], but it clearly manifests itself experimentally by decreasing the Fermi hyperfine coupling of H

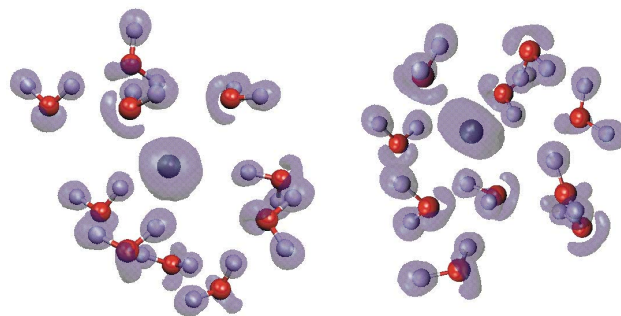


FIG. 2 (color online). Spin-polarized electron localization function $\eta(\mathbf{r})$ for the first solvation shell cluster of H^* at the contour value $\eta^* = 0.88$. Only the chemically relevant valence electrons are included in the ELF analysis. In the left and in the right panel the H^* atom is close to or far from the instantaneous center of the cavity, respectively.

isotopes in water relative to the isotropic vacuum reference as measured by EPR/ μ SR spectroscopy [35].

Turning now to the dynamics, the mean-square displacement of the water molecules is compared to that of H^* in Fig. 4. Although the present trajectory is clearly too short to yield very accurate (self-) diffusion coefficients D , we roughly estimate $D_{H_2O} \approx 3.8 \times 10^{-9} \text{ m}^2/\text{s}$; note that all nuclei are treated as classical point particles and that the deuterium mass is used for technical reasons [32]. This compares reasonably to the experimental values [22] $D_{H_2O}^{\text{exp}} = 3.39 \times 10^{-9} \text{ m}^2/\text{s}$ and $D_{D_2O}^{\text{exp}} = 2.83 \times 10^{-9} \text{ m}^2/\text{s}$ for normal and heavy bulk water at 315 K. However, a big surprise is the magnitude of D for the solute H^* : it is as large as $D_H \approx 7.7 \times 10^{-9} \text{ m}^2/\text{s}$ at 315 K and thus exceeds the one of the solvent D_{H_2O} by a factor of about 2. This enhancement is consistent with experiments [20] where $D_H^{\text{exp}}/D_{H_2O}^{\text{exp}} \approx 3$ and $D_D^{\text{exp}}/D_{D_2O}^{\text{exp}} \approx 2$ at 298 K.

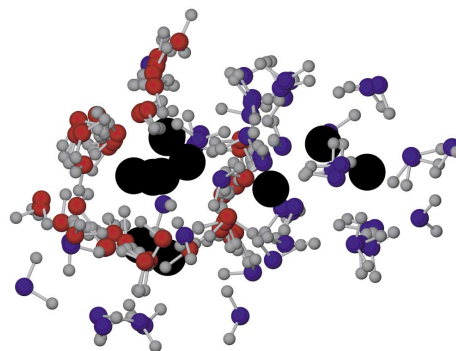


FIG. 3 (color online). Superimposed snapshots of H^* and its instantaneous solvation shell (chosen to be the ten closest water molecules) for one typical full exchange of the solvation shell thus including 11 configurations. Those water molecules that solvate H^* (large black sphere) in the first configuration stay colored in red, whereas every exchanged water molecule is marked in blue.

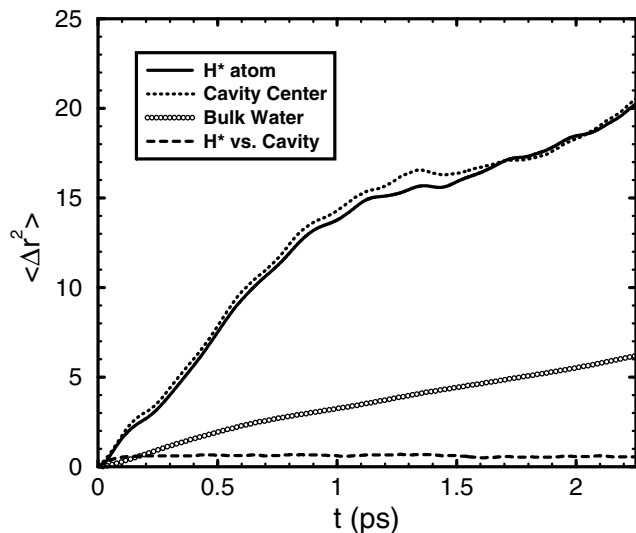


FIG. 4. Mean-square position displacements as a function of time for the H^* atom (solid line), the center of the cavity (dotted line), “bulk” water (open circles), and H^* relative to the center of the cavity (dashed line).

Thus, our *ab initio* simulations reproduce also the anomalously fast *dynamics* of the solvated H atom in water. We note in passing that similar enhancements of diffusion coefficients were also found in computer “experiments” after discharging model cations in SPC/E water while keeping the mass identical [16].

How is it possible that the hydrated H atom can diffuse so fast? A first hint can be obtained from the fact that the “diffusion coefficient” of the cavity center, $D_{\text{cav}} \approx 6.7 \times 10^{-9} \text{ m}^2/\text{s}$, is very similar to D_{H} ; D_{cav} was obtained by following the instantaneous center of mass of the ten water molecules closest to H^* . Furthermore, the mean-square displacement of the H atom relative to the cavity center levels off after about 200 fs, see Fig. 4, and reaches a constant value of about 0.6 \AA^2 , which is the Debye-Waller factor of the bound rattling motion of H^* in its cavity. The trajectory in Fig. 3 uncovers that the water molecules in the first solvation shell exchange quite rapidly one after the other. The average time needed for such full exchanges is about 1.4 ps. After such a complete resolution the H atom has traveled over a *net* distance of about $6.6 \pm 0.6 \text{ \AA}$ on the average. This scenario is very different from what is observed for small hydrated cations [19] that travel for many picoseconds with their hydration shell *attached*. In these cases the residence times of solvation water are large which supports the classical “solventberg” picture [16]. On the other hand, the fast dynamics of the H atom with similarly large displacements per event can indeed be observed for protons H^+ in water [23], a system that is, however, chemically completely different from the H atom. Thus, the emerging picture is that of an H atom that migrates rapidly *because* of the fluctuations in the hydrogen-

bonding network of its hydration shell, which results in fast water molecule exchanges and thus dynamical shape changes. This process can be viewed as a “structural diffusion mechanism” like that of fast proton diffusion [23]. However, in the H atom case the diffusing “structure” is a topological defect, the cavity, whereas it is a charge defect in the H^+ case, the H_3O^+ ion. Very interestingly, the uncovered mechanism is very similar in character to the dynamical hole mechanism that is operational for the diffusion of larger molecules (as opposed to atoms or small molecules) in polymeric melts at high temperatures via anisotropic fluctuations of solute-containing cavities in the polymeric matrix on short time scales [36].

The present finding might be related to the discovery that pure bulk water is characterized by an *equilibrium* concentration of “hydrophobic cavities” or “voids” that are *spontaneously* created and destroyed due to thermal fluctuations [37]. Recently, the resulting *intercavity* correlations were even found to explain the so-called “pre-peak” or “first-sharp-diffraction peak” [38], which is experimentally observable. Most interestingly, the cavity center-O and -H radial distribution functions were found [37] to peak around 3.0 \AA and 2.8 \AA , respectively, which can be interpreted as the preferred cavity size in liquid water. This is intriguingly close to the present cavity radius of H^* given by the maxima of $g_{\text{H}^*\text{O}}$ and $g_{\text{H}^*\text{H}}$ at 3.0 \AA and 2.9 \AA , respectively. In other words the spontaneously occurring cavities in liquid water appear to have just the right size for hosting a *small* solute, such as the H atom. Based on these observations, one is tempted to speculate that anomalously fast diffusion of small hydrophobic species in water is possible because (i) these solutes can populate preferred cavity sizes and (ii) the diffusion of the solute is driven by fast water exchanges in the cavity due to fluctuations of the hydrogen-bonding network.

In summary, these *ab initio* MD simulations do not support the notion of a *frozen* iceberglike clathrate cage around the hydrophobic H atom; a recent neutron study also challenges this picture based on independent arguments [19]. On the contrary, a surprisingly floppy or fluxional solvation shell actually *promotes* the anomalously fast diffusion of small hydrophobic solutes (such as H atoms) in water that shows up in experiments [20]. A simple atomistic picture of the underlying process would be that of the hydrophobic solute following the fast motion of its cavity, which in turn is driven by rapid water exchanges due to hydrogen-bond fluctuations.

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