

## Relations between the diffusion anomaly and cooperative rearranging regions in a hydrophobically nanoconfined water monolayer

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We simulate liquid water between hydrophobic walls, separated by 0.5 nm, to study how the diffusion constant  $D_{\parallel}$  parallel to the walls depends on the microscopic structure of water. At low temperature  $T$ , water diffusion can be associated with the number of defects in the hydrogen bond network. However, the number of defects solely does not account for the peculiar diffusion of water, with maxima and minima along isotherms. Here, we calculate a relation that quantitatively reproduces the behavior of  $D_{\parallel}$ , focusing on the high- $T$  regime. We clarify how the interplay between breaking of hydrogen bonds and cooperative rearranging regions of 1-nm size gives rise to the diffusion extrema in nanoconfined water.

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In normal liquids the diffusion constant  $D$  decreases when the pressure  $P$  increases at constant temperature  $T$ . Water, instead, displays up to a 60% increase of  $D$  [1] for  $P < 200$  MPa [2]. Based on simulations of bulk water with detailed models, e.g., Refs. [3–5], and lattice models, e.g., Ref. [6], relations between the behavior of  $D$  and the structure of water have been proposed. For example,  $D$  can be related to the configurational entropy [7], and the minima in  $D$  can be associated with a maximum in orientational order [8]. In classical molecular dynamics (MD) simulations an increase of  $P$  weakens the hydrogen bonds (HBs), thus increasing  $D$  [4]. This interpretation in terms of defects in the HB network can be extended to negative  $P$  [5]. A similar qualitative conclusion has been reached also by *ab initio* MD [9]. Nevertheless, a quantitative relation between the microscopic structure of water and the anomalous behavior of  $D$ , including both extrema, is still missing.

Diffusion experiments in hydrophobic confinement are at issue. For water confined in carbon nanotubes (CNTs) with diameters from 5 to 2 nm,  $D$  decreases for smaller diameters [10]. Nevertheless, other experiments reveal an exceptionally fast transport for water confined in CNTs of  $\sim 2$  [11] and 7 nm diam [12].

Results from models are also controversial. MD simulations of five point transferable intermolecular potential (TIP5P) water nanoconfined between hydrophobic smooth walls display an anomalous diffusion constant  $D_{\parallel}$  parallel to the walls at lower  $T$  than in bulk [13], and no anomaly in the orthogonal direction [14]. A large decrease of diffusion is found at ambient conditions for extended simple point charge (SPC/E) water between two large hydrophobic graphitelike plates for separations below 1.3 nm [15]. Nevertheless, first-principles MD of the same model in similar conditions show that the diffusion becomes faster under confinement, possibly due to weaker HBs at the interface [16]. A similar controversy is reported for simulations of water in CNTs, with diameters below 1 nm [16–18].

Here we study, by the Monte Carlo (MC) method, the diffusion of water in a monolayer between two parallel hydrophobic walls, adopting an already well-studied coarse-grained model [19]. We find maxima and minima of  $D_{\parallel}$  and

derive an expression that relates  $D_{\parallel}$  to water configurations, identifying cooperative rearranging regions and a relation among structure, thermodynamics, and dynamics that clarifies the mechanisms for water diffusion.

We consider two flat hydrophobic walls at a distance of  $h \simeq 0.5$  nm such that the formation of ice is inhibited [20]. Adopting the natural square symmetry of the system [20], we divide the available volume  $V$  into  $\mathcal{N}$  square cells, each with a volume  $v = V/\mathcal{N}$ , and hydrate the system with  $N \leq \mathcal{N}$  water molecules. To each cell we associate an occupation variable  $n_i = 0, 1$  ( $i = 1, 2, \dots, \mathcal{N}$ ) if it is vacant or occupied, respectively. The enthalpy of the system is

$$H \equiv \sum_{ij} U(r_{ij}) - JN_{\text{HB}} - J_{\sigma} \sum_i n_i \sum_{(k,\ell)_i} \delta_{\sigma_{ik}, \sigma_{i\ell}} + PV, \quad (1)$$

where  $r_{ij}$  is the distance between water molecules  $i$  and  $j$ ,  $U(r) \equiv \infty$  for  $r < r_0 \equiv 2.9$  Å, the water van der Waals diameter,  $U(r) \equiv \epsilon_w [(r_0/r)^{12} - (r_0/r)^6]$  for  $r \geq r_0$  with  $\epsilon_w \equiv 5.8$  kJ/mol, the isotropic attraction energy, and  $U(r) = 0$  for  $r > r_c = \sqrt{\mathcal{N}}/4$ , the cutoff distance.  $J \equiv 2.9$  kJ/mol is the characteristic energy of the directional (covalent) component of the HB [21],  $N_{\text{HB}} \equiv \sum_{(i,j)} n_i n_j \delta_{\sigma_{ij}, \sigma_{ji}}$  is the total number of HBs, where the sum is over nearest-neighbor (n.n.) molecules,  $\delta_{\sigma_{ij}, \sigma_{ji}} \equiv 1$  if  $\sigma_{ij} = \sigma_{ji}$ ,  $\delta_{\sigma_{ij}, \sigma_{ji}} \equiv 0$  otherwise, and the variables  $\sigma_{ij}$  are defined as follows. We adopt a geometrical definition in which the HB breaks if  $\angle \text{OOH} > 30^\circ$ . Therefore, only 1/6 of the orientation range  $[0, 360^\circ]$  in the OH-O plane is associated with a bonded state. Hence, we account for the entropy loss of molecule  $i$  due to the formation of a HB with molecule  $j$  by associating to  $i$  a bonding index  $\sigma_{ij}$ , and to  $j$  a bonding index  $\sigma_{ji}$ , with both indices  $\in [1, 2, \dots, q]$  with  $q \equiv 6$ . For the square symmetry, each molecule has four n.n. and four  $\sigma_{ij}$ , with  $q^4 = 6^4 = 1296$  possible bonding states. Therefore, when two n.n. molecules  $i$  and  $j$  with  $n_i n_j = 1$  form a HB, their energy and entropy decrease.

HB formation increases the average volume per molecule, because it induces a local structure with a reduced number of n.n. as compared to close packing [22]. This effect is accounted for by an enthalpy increase  $Pv_{\text{HB}}$  for each HB, where  $v_{\text{HB}}/v_0 \equiv 0.5$  is the average density increase from low-density ice Ih to high-density ices VI and VIII, and  $v_0 \equiv hr_0^2$ .

The total volume occupied by water is  $V_w \equiv Nv + N_{\text{HB}}v_{\text{HB}}$ . The increase  $v_{\text{HB}}$  corresponds to a larger volume per molecule, but not to a larger separation  $r$  between molecules, having no effect on  $U(r)$ .

In Eq. (1),  $J_\sigma \equiv 0.29$  kJ/mol is the energy gain for two bonding indices of the same molecule in the same state, and accounts for the HB many-body (cooperative) interaction [2,19], with the sum over  $(k,\ell)_i$ , i.e., over each of the six different pairs of the four  $\sigma_{ij}$  of a molecule  $i$ . This cooperative interaction among HBs favors specific  $T$ - and  $P$ -dependent values of the probability distribution of O-O-O angles [23]. In confinement, the distribution displays no fifth interstitial n.n. and has a maximum shifted toward  $90^\circ$  at low  $T$  [24], consistent with the square symmetry adopted here. The water-wall interaction is represented by a hard-core exclusion.

We perform MC simulations in the  $NPT$  ensemble for  $\mathcal{N} = 2500$  and  $N/\mathcal{N} = 0.75\%$ , corresponding to  $N = 1875$  water molecules. Since we allow for changes of the volume in the direction parallel to the walls, the control parameter  $P$  represents the pressure parallel to the walls. We test that for  $\mathcal{N} = 400$  and  $1600$  at the same  $75\%$  occupancy ratio there are no appreciable differences, as well as for  $75\% \leq N/\mathcal{N} \leq 90\%$ . The detailed MC algorithm and the conversion to real units are described elsewhere [19]. We equilibrate each state point for  $0.2$  ms and average over  $15$  ms [25].

We calculate  $D_{\parallel}$  from the two-dimensional Einstein relation

$$D_{\parallel} = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}_i(t + t_0) - \mathbf{r}_i(t)|^2 \rangle}{4t}, \quad (2)$$

where  $\mathbf{r}_i(t)$  is the projection onto the plates of the position of molecule  $i$  at time  $t$ , and  $\langle \cdot \rangle$  is the average over all molecules  $i$  and over different values of  $t_0$ . We find that  $D_{\parallel}$  decreases below a maximum  $D_{\parallel}^{\text{max}}$  for decreasing  $P$ , with a maximum at  $P^{\text{max}} \lesssim 0.2$  GPa, as in bulk water [2], reaching a minimum  $D_{\parallel}^{\text{min}}$  at  $P^{\text{min}} \leq P^{\text{max}}$  (Fig. 1).  $P^{\text{min}}$  decreases with decreasing  $T$  and eventually becomes negative. For the high temperatures considered here,  $D_{\parallel}$  is smaller than the diffusion constant for

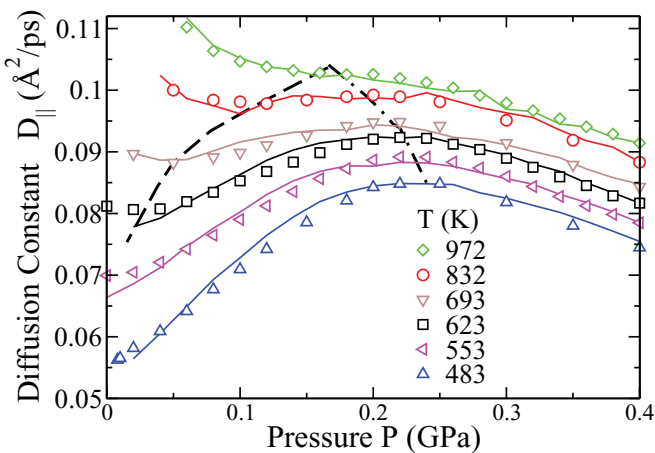


FIG. 1. (Color online) Diffusion coefficient  $D_{\parallel}$  from MC simulations (symbols) as a function of pressure along isotherms for (from top to bottom)  $T$  between 972 and 483 K. For  $T < 972$  K,  $D_{\parallel}$  has maxima  $D_{\parallel}^{\text{max}}$  at  $P^{\text{max}}$  (dotted-dashed line) and minima  $D_{\parallel}^{\text{min}}$  at  $P^{\text{min}}$  (dashed line). Solid lines are from Eq. (6), as described in the text.

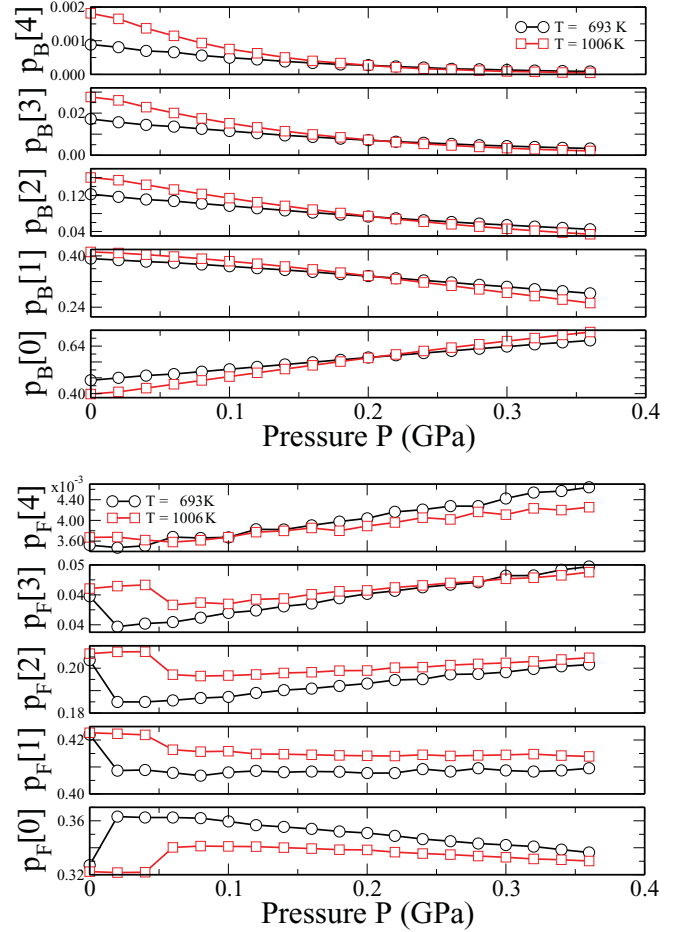


FIG. 2. (Color online) Microscopic configuration changes along isotherms for temperatures 1006 K (squares) and 693 K (circles), corresponding to the onset of anomalous  $D_{\parallel}$  and to the fully developed anomaly of  $D_{\parallel}$ , respectively. Top: Probability  $p_B[i]$  for a molecule to participate in  $i = 0, \dots, 4$  HBs. Bottom: Probability  $p_F[i]$  for a molecule to have  $i = 0, \dots, 4$  free n.n. cells available for diffusion. The discontinuity in  $p_F[i]$  corresponds to the liquid-gas first-order phase transition. Among different panels, probability values change up to two orders of magnitude.

bulk water, qualitatively consistent with high- $T$  simulations of water in CNTs [17].

To quantitatively relate the anomalous behavior of  $D_{\parallel}$  with the microscopic arrangement of water molecules, we define  $p_B[i]$  as the probability for a molecule to participate in (exactly)  $i$  HBs, with  $i = 0, \dots, 4$ , and  $p_F[i]$  as the probability for a molecule to have (exactly)  $i$  free n.n. cells available for diffusion (Fig. 2). By definition  $\sum_i p_B[i] = \sum_i p_F[i] = 1$  and  $p_d \equiv 1 - p_B[4]$  is the probability to have defects in the HB network. Because  $p_B[4]$  is a monotonic function also for temperatures at which  $D_{\parallel}$  is nonmonotonic, our result shows clearly that the network defects cannot be solely responsible for anomalous water diffusion.

In particular, the probabilities  $p_B[i]$  behave regularly for any  $i$  (Fig. 2). The probability  $p_B[0]$  of a molecule not participating in any HB increases by increasing  $P$ , because of the enthalpic cost of forming HBs at high  $P$ . For the same

reason, the other  $p_B[i]$  to form  $i > 0$  HBs decrease with  $P$ , being vanishing small for  $i = 3$  and 4.

Moreover, the behavior of  $p_F[i]$  is regular within the liquid phase, with the probability  $p_F[0]$  to have 0 free n.n. cells (high density) increasing discontinuously at the gas-liquid phase transition. Although  $p_F[0]$  decreases by increasing  $P$  in the liquid phase, it is always larger than in the gas phase. The decrease of  $p_F[0]$  is compensated by increases in  $p_F[2]$ , while  $p_F[1]$  is almost constant in the liquid phase and  $p_F[3]$  and  $p_F[4]$  are vanishing small. We understand the small increase of  $p_F[3]$  and  $p_F[4]$  as a consequence of the phase separation between liquid and gas, favored by the breaking of HBs due to the increase of  $P$ . By comparing two different temperatures, we find that at any  $P$  the higher  $T$  has lower  $p_F[0]$ , consistent with its lower density (Fig. 2).

Therefore, none of the quantities  $p_B[i](P)$  or  $p_F[i](P)$  shows an evident nonmonotonic behavior in the liquid phase that could be unambiguously related to the nonmonotonic behavior of  $D_{\parallel}(P)$ . In the liquid phase, we also find a regular behavior for the average number of free n.n. cells around a molecule,  $\langle n_F \rangle \equiv \sum_{f=0}^4 f p_F[f]$ , and for the average number of HBs formed by a molecule,  $\langle n_{HB} \rangle \equiv \sum_{b=0}^4 b p_B[b]$  (inset in Fig. 3).

We observe (Fig. 3) that at 693 K, for  $P$  decreasing from 0.4 GPa to approximately atmospheric pressure, the average number of HBs per molecule  $\langle n_{HB} \rangle$  increases from 0.3 to  $\approx 0.8$ , while the average number of free n.n. cells,  $\langle n_F \rangle$ , around each molecule has a small decrease from 1 to 0.9. Hence, by decreasing  $P$ , the change in HBs is large, but not the reduction of free volume around each molecule.

Nevertheless, diffusion in a liquid is a process that involves more than one molecule at a time, as a consequence of the

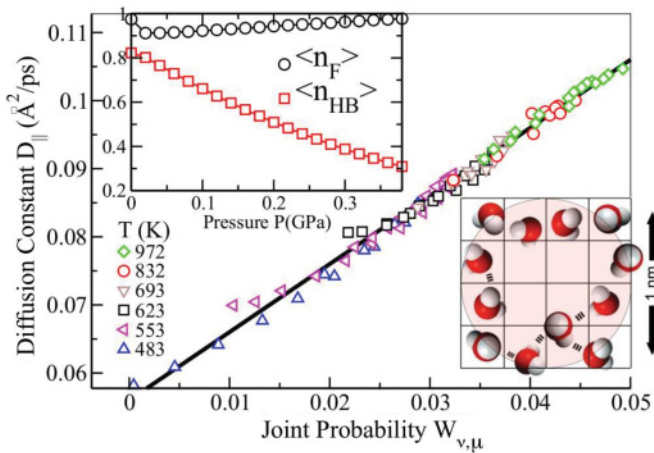


FIG. 3. (Color online) Upper inset: Average numbers of free n.n. cells around a molecule  $\langle n_F \rangle$  (circles) and of HBs formed by a molecule  $\langle n_{HB} \rangle$  (squares) as a function of  $P$  at  $T = 693$  K. The discontinuity in  $\langle n_F \rangle$  at low  $P$  corresponds to the gas-liquid first-order phase transition. At higher  $P$ , both quantities are monotonic. Main panel: The plot of  $D_{\parallel}$  vs  $W_{\nu, \mu}$  along the six isotherms represented in Fig. 1 shows that  $D_{\parallel}$  is a linear function of  $W_{\nu, \mu}$  within the numerical noise. The parameters  $\nu$  and  $\mu$  change with  $T$ , as described in the text. Lower inset: Example of a cooperative (shaded) region of  $\sim 1$  nm size, with  $\nu = 12$  molecules with n.n. free cells (not all represented in the scheme) and  $\mu \mathcal{P}_b = 5$  HBs.

cooperative displacement of molecules, especially at high densities [26]. Therefore, what is relevant is not just the available volume around a molecule, but the volume available for diffusion  $V_{DA}$  (dynamically available volume) over a region large enough to allow for cooperative movement of the molecules in it [26].

To find an analytic expression for quantifying the balance of  $V_{DA}$  and broken HBs necessary for diffusion, we observe that for a microscopic configuration with averages  $\langle n_F \rangle$  and  $\langle n_{HB} \rangle$  (both functions of  $P$  and  $T$ ), the enthalpy per molecule Eq. (1) is, in mean-field approximation,

$$H(P, T) \equiv H\{\langle n_F \rangle, \langle n_{HB} \rangle\} \\ \equiv -\epsilon(4 - \langle n_F \rangle) - (J - P v_{HB}) \langle n_{HB} \rangle, \quad (3)$$

where we assume that the average contribution of the cooperative term in Eq. (1) is negligible in the considered range of  $P$ - $T$ , as suggested by our calculations [19].

Defining  $\mathcal{P}_F \equiv \langle n_F \rangle / 4$  as the probability for each cell to have a n.n. cell that is free, and  $\mathcal{P}_b \equiv \langle n_{HB} \rangle / 4$  as the probability for each possible HB to be formed, the quantity

$$W(P, T) \equiv \mathcal{P}_F \mathcal{P}_b \frac{1}{Z} \exp[-H(P, T)/(k_B T)] \quad (4)$$

is the joint probability that, at a given  $P$  and  $T$ , a molecule forms a HB and has a free n.n. cell, with

$$Z \equiv \sum_{f=0}^4 \mathcal{P}_F[f] \sum_{b=0}^{4-f} \mathcal{P}_b[b] \exp[-H\{f, b\}/(k_B T)], \quad (5)$$

where  $H\{f, b\}$  is given by Eq. (3). The generalization of  $W(P, T)$  is

$$W_{\nu, \mu}(P, T) \equiv \mathcal{P}_F^{\nu} \mu \mathcal{P}_b \frac{1}{Z} \exp[-H(P, T)/(k_B T)], \quad (6)$$

and represents the probability, at given  $P$  and  $T$ , of finding  $\nu$  molecules with a n.n. free cell available for diffusion within a region with  $\mu \mathcal{P}_b$  HBs (lower inset in Fig. 3). If the diffusion behavior is dominated by the cooperative rearrangement of molecules within a given region of the system, then  $D_{\parallel}$  must be directly proportional to  $W_{\nu, \mu}$  for some values of  $\nu$  and  $\mu$ .

A comparison with our MC simulations confirms this hypothesis (Fig. 3). We find that, within the numerical noise,  $D_{\parallel} = \tilde{D} W_{\nu, \mu} + D_0$ , where  $\tilde{D} = 1 \text{ \AA}^2/\text{ps}$ . The parameters  $\nu$ ,  $\mu$ , and  $D_0$  depend only on  $T$ , with the first two describing the cooperative rearranging region and the last associated with the case  $\mu = 0$ , i.e., with the diffusion constant at high  $P$ . In particular, we find  $D_0 \lesssim 0.03 \text{ \AA}^2/\text{ps}$ , consistent with the observation that, at very high  $P$ , water recovers a normal behavior and the diffusion is extremely small. For the range of  $P$ - $T$  where we observe the diffusion anomaly, we find  $\nu = 12.5 \pm 0.5$  and  $\mu$  decreasing from  $15 \pm 1$  at  $T = 483$  K to  $\simeq 4 \pm 3$  for  $T \geq 623$  K. The resulting  $\nu = 12.5$  suggests that for the water monolayer between hydrophobic walls the diffusion mechanism, in the studied  $P$ - $T$  range, requires a cooperative rearranging region that extends over  $\sim 3.5$  water molecules, corresponding to  $\sim 1$  nm (lower inset in Fig. 3). The outcome for  $\mu$  conveys that at lower  $T$  almost all the HBs,  $\sim 18$ , within this cooperative rearranging region need to be broken to allow for macroscopic diffusion, while at higher  $T$  the number of broken HBs necessary for diffusion rapidly

decreases as a consequence of the reduced number of formed HBs (Fig. 2).

In conclusion, the result of our analysis is twofold. On the one hand, it clarifies the mechanisms inducing the diffusion anomaly. In particular, it shows that at constant  $T$ , by increasing  $P$ , the number of HBs ( $n_{\text{HB}}$ ) decreases, implying a decrease of the energy cost for a molecule to move and an increase of free volume, proportional to  $\langle n_F \rangle$ , available for diffusion and competing with the decrease of free volume due to the increase of density. These competing mechanisms cause the increase of diffusion under pressurization at low  $P$  and their combined effect reaches a maximum at a pressure above which HB formation is unfavorable for enthalpic reasons. For the conditions considered here (high  $T$  and strong hydrophobic confinement),  $D_{\parallel}$  is reduced with respect to bulk. On the other hand, our calculations give a quantitative description of the phenomenon and show that the competition between free volume, available for diffusion, and the formation and breaking of HBs occurs within a cooperative region of approximately

three water molecules, or 1 nm, in the  $P$ - $T$  range relevant for diffusion anomaly in a hydrophobically nanoconfined monolayer of water. This result recalls the finding of Ref. [27], where the size of cooperatively rearranging regions is estimated to be of the order 1 nm for a large number of glass-forming materials close to the glass temperature. Here, the 1-nm size is found at  $T$  higher than the bulk glass temperature, consistent with the fact that  $D_{\parallel}$  in confinement is reduced with respect to bulk. Finally, the fact that simulations for water confined between graphitelike plates [15] or CNTs [18] show a large decrease of diffusion when the confining length scale is below 1 nm, suggests that strong confinements of water interfere with the cooperative rearrangement necessary for diffusion. Here the 1-nm scale emerges as a natural length associated with the diffusion mechanism.

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