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Hydrogen-bond dynamics of water in a quasi-two-dimensional hydrophobic nanopore slit

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We perform molecular dynamics simulations to investigate hydrogen-bond dynamics of the TIP5P (transferable intermolecular potential with five points) model of water confined in a quasi-two-dimensional hydrophobic nanopore slit. We find that even if the average number and the lifetime of hydrogen bonds are affected by nanoconfinement, the characteristics of hydrogen-bond dynamics in hydrophobic confined water are the same as in bulk water—such as an Arrhenius temperature dependence of average hydrogen-bond lifetime and a nonexponential behavior of lifetime distributions at short time scales. The different physical properties of water in hydrophobic confinement compared to bulk water—such as ~40 K temperature shift—may be primarily due to the reduction of the lifetime of hydrogen bonds in confined environments. We also find that the hydrogen-bond autocorrelation function exhibits a power-law tail following a stretched exponential behavior. The relaxation time of hydrogen bonds in confined water is smaller than in bulk water. Further, we find that the temperature dependence of the relaxation time follows a power-law behavior, and the exponents for bulk and confined water are similar to each other.

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Since the first description of a hydrogen bond (HB) almost 90 years ago [1], it has been generally believed that the forming and breaking of HBs play an important role in the distinctive properties of water [2]. Many experiments [3–7] and simulations [8–16] have focused on understanding the characteristic properties of HB dynamics in bulk water, such as the average lifetime, the structural relaxation time, and the HB autocorrelation functions. Previous studies on bulk water showed that the distribution of HB lifetimes exhibits a nonexponential behavior at short time scales followed by an exponential behavior at long time scales, suggesting that a HB relaxation is not a simple process [9,10,12].

Confined water generally shows thermodynamic, structural, and dynamical properties different from bulk water due to the geometric constraints and the interactions with confining surfaces [17–20]. Previous studies have shown that for hydrophobically confined water the anomalous diffusive motion is shifted to lower temperatures by about 40 K compared to bulk water [18,19], and the diffusion anomaly in bulk water may be absent [20]. Confined water is also useful for testing the hypothesized liquid-liquid phase transition scenario [21,22], since nanoconfinement prevents water from crystallizing down to very low temperatures. An open question is how much the properties of confined water will change relative to bulk water, and what gives rise to these differences.

Previous HB studies in confined systems showed that compared to bulk water the HB relaxation time τ_R in water confined in micelles [6,23], as well as at vapor-water and metal-water interfaces [24], is longer. For water confined to the interior of carbon nanotubes, the HB lifetime becomes longer [25] or shorter [26] than that in bulk water, depending on the conditions in the system. Although many believe that the differences between confined water and bulk water are ascribed to changes in HB properties, HB dynamics in confined water is far from being fully understood [27]. In this paper, we will investigate HB dynamics confined in a quasi-two-dimensional hydrophobic nanopore slit.

We perform molecular dynamics (MD) simulations of $N=512$ TIP5P (transferable intermolecular potential with five points) [28,29] waterlike molecules confined between two infinite parallel smooth plates, separated by a distance $L_z=1.1$ nm, which are able to contain two to three layers of water molecules. We model the water-wall interaction by a 9-3 Lennard-Jones (LJ) potential and choose LJ parameters to have hydrophobic properties, as in Refs. [18,20]. We perform MD simulations for a fixed water density $\rho=1.02$ g/cm^3 and for eight temperatures from 300 K down to 230 K. The density for confined water is calculated by considering the accessible space between plates, as explained in Ref. [18]. Periodic boundary conditions are used in x and y directions. For the sake of comparison, we also perform MD simulations of bulk TIP5P water for a density of $\rho=1.00$ g/cm^3 and for the same eight temperatures as in confined water. To study HB dynamics, we use the geometric definition of HB, which is that two tagged molecules are considered to be bonded if simultaneously their interoxygen distance is less than 3.5 Å, and the angle between intra O-H and inter O$\cdots$O is less than 30° [10,12].

First, we calculate $\langle n_{\mathrm{HB}}\rangle$, the average number of HBs, in both confined and bulk water for different temperatures (Fig. 1). We find that because of the geometric constraints, the tetrahedral structure of the HB network in water is not favorable in confined space. Also, we find that due to the hydrophobic property of the confining surface, the number of HBs in confined water is smaller than in bulk water. In Fig. 1, we show that $\langle n_{\mathrm{HB}}\rangle$ in hydrophobically confined water is about 88% of $\langle n_{\mathrm{HB}}\rangle$ in bulk water, consistently over all temperatures investigated. This reduction of $\langle n_{\mathrm{HB}}\rangle$ is also consistent with the experimental fact that confined water freezes at lower temperature compared to bulk water [30].

Next, we calculate the probability density function (PDF) $P(t)$ of the HB lifetimes in both confined and bulk water (Fig. 2). In previous studies of bulk water, $P(t)$ shows a nonexponential behavior at short time scales [9,12], suggesting that forming and breaking of HB is not a simple process.

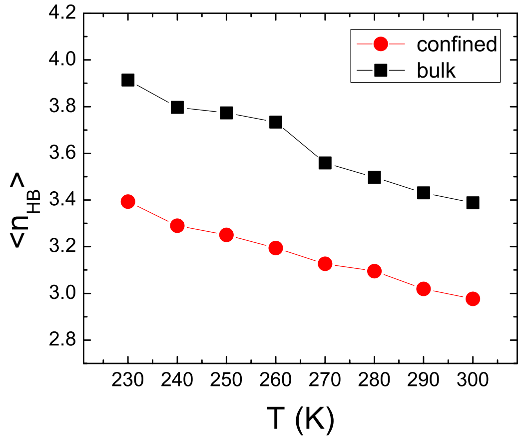

FIG. 1. (Color online) The average number of hydrogen bonds per water molecule, $\langle n_{\mathrm{HB}} \rangle$, as a function of temperature. For both confined and bulk water, $\langle n_{\mathrm{HB}} \rangle$ decreases as temperature increases. Due to the geometric constraints and the hydrophobic property, $\langle n_{\mathrm{HB}} \rangle$ is smaller in confined water than in bulk water.

However, Luzar [13] studied the behavior of $P(t)$ using two different HB definitions—strict and less strict HB definitions—and then concluded that $P(t)$ follows an exponential behavior by matching the long-time nonexponential relaxation function. Moreover, Luzar [13] presented in a figure that there are two different behaviors in $P(t)$, a nonexponential part (for $t < 2$ ps) followed by an exponential tail, and the average HB lifetime calculated by Luzar [13] is around 0.2–0.4 ps for both HB definitions. Therefore, it is natural to conclude that $P(t)$ follows a nonexponential behavior followed by a long-time exponential tail. Whether or not the initial nonexponential behavior of $P(t)$ is actually a power-law behavior [9,12,13,31] is also an interesting problem, but it is beyond the scope of the present work.

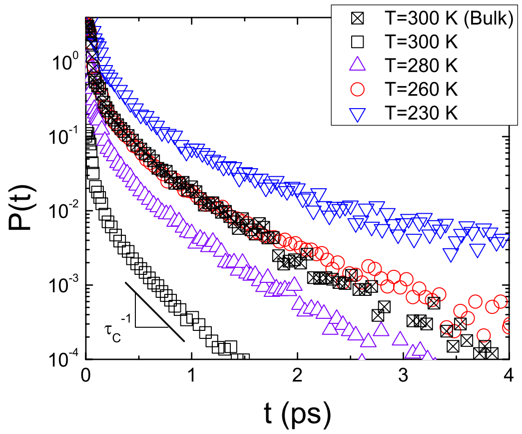

FIG. 2. (Color online) Shown in a semilogarithmic plot are the distributions $P(t)$ of hydrogen-bond lifetimes t at different temperatures. The plots, except $T=300$ K for confined water, are shifted up for clarity. $P(t)$ indicates that there is a region which shows a nonexponential behavior, followed by an exponential tail for all temperatures investigated. Note that $P(t)$ for $T=260$ K for confined water and $T=300$ K for bulk water overlap, corresponding to the 40 K shift proposed in Refs. [18,19,32] for hydrophobic confinement. The line segment has slope τ_C^{-1} (see Fig. 3), since $P(t) \sim \exp(-t/\tau_C)$ in long time scales.

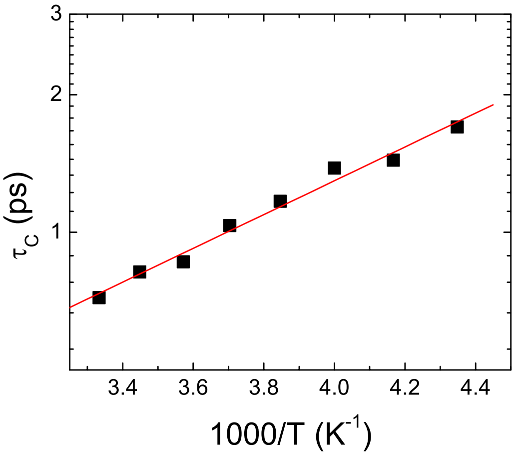

FIG. 3. (Color online) Shown in an Arrhenius plot is the characteristic time τ_C of the exponential tail in $P(t)$ [$\sim \exp(-t/\tau_C)$] as a function of temperature for confined water. It shows that the temperature dependence of τ_C can be fitted by an Arrhenius form (line).

In Fig. 2, we find that $P(t)$ in confined water decays slightly faster than in bulk water at the same temperature. The nonexponential behavior followed by an exponential tail of $P(t)$ is preserved as in the case of bulk water. However, we find that $P(t)$ of bulk water overlaps $P(t)$ for confined water when the bulk temperature is ~40 K higher than the confined temperature. This shift in PDF of lifetime may be the origin of reasons for the shift of temperature ($\Delta T \sim 40$ K), at which anomalous thermodynamic behaviors appear, found in a simulation of hydrophobically confined water [18,19] and also temperature shift ($\Delta T \sim 35$ K) of dynamic crossover experimentally found for water confined in carbon nanotubes [32]. Since $P(t)$ has an exponential tail, one can calculate the characteristic time τ_C defined by $P(t) \sim \exp(-t/\tau_C)$ at long time scales. In Fig. 3, we show that the temperature dependence of τ_C can be fitted by an Arrhenius form.

In Fig. 4, we calculate in both confined and bulk water the average HB lifetimes

$$\tau_{\mathrm{HB}} \equiv \int_0^\infty tP(t)dt. \qquad (1)$$

We define τ_{HB} as the *continuous* HB lifetime [11], which means that HB remains intact during this time. Generally, τ_{HB} represents *fast* motion of HB related to the librational motion [12]. In Fig. 4, we show τ_{HB} as a function of temperature for both bulk and confined water. We find the temperature dependence of τ_{HB} is an Arrhenius one, described by $\tau_{\mathrm{HB}} = \tau_0 \exp(E_A/k_B T)$. Notice that τ_{HB} for both bulk and confined water has an Arrhenius dependence on temperature, but with different activation energy E_A, which has been interpreted as the energy required to break a HB via librational motion [12]. Further, we find that the activation energy E_A of confined water ($E_A^C = 4.92 \pm 0.07$ kJ/mol) is about half that in bulk water ($E_A^B = 9.80 \pm 0.53$ kJ/mol) [33]. As a result, τ_{HB} in confined water is smaller than in bulk water at the same temperature. As for the PDF of HB lifetime, $\tau_{\mathrm{HB}}(T)$ in

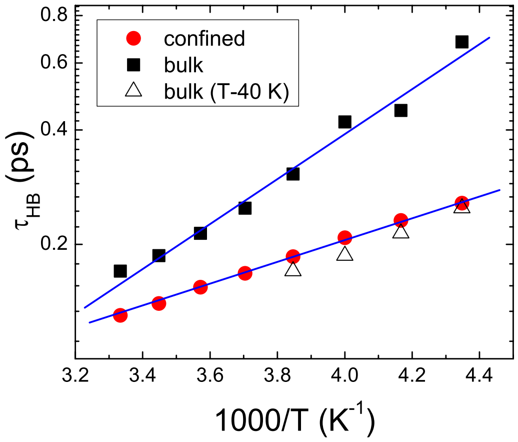

FIG. 4. (Color online) The average HB lifetime τ_{HB} as a function of $1/T$ in an Arrhenius plot. Two blue lines indicate the fits, $\tau_{\mathrm{HB}}=\tau_0 \exp(E_A/k_BT)$. For confined water, τ_{HB} can be fitted by an Arrhenius behavior, which is preserved as in bulk water, even if τ_{HB} and the number of hydrogen bonds in confined water are smaller than in bulk water. The magnitude of activation energy calculated for confined water ($E_A^C=4.92\pm0.07$ kJ/mol) is around half of that in bulk water ($E_A^B=9.80\pm0.53$ kJ/mol). E_A^B is consistent with previous experimental and simulation results for the activation energy associated with fast hydrogen-bond dynamics. The triangle symbols are for bulk water at temperatures shifted lower by $\Delta T=40$ K.

bulk water can be matched to $\tau_{\mathrm{HB}}(T)$ in confined water by shifting to lower temperature by 40 K, suggesting that the origin of the temperature shift in thermodynamic properties in confined water may be due to the change in the HB lifetime. However, $\langle n_{\mathrm{HB}}\rangle$ in bulk water is *not* the same as that in confined water when temperature is shifted downward by $\approx$40 K, as shown in Fig. 1. Note that the match of HB lifetimes by 40 K temperature shift will be restricted in a certain range of temperatures (here it is a supercooled regime for confined water), since the slopes in Fig. 4 are slightly different when they are shifted by 40 K.

To investigate the slow kinetics of HBs, we calculate the relaxation time τ_R from the HB autocorrelation function [10–16]

$$c(t) \equiv \frac{\langle h(0)h(t)\rangle}{\langle h\rangle}. \tag{2}$$

Here $h(t)$ is unity when two tagged molecules are hydrogen bonded at time t and is zero otherwise. This function $c(t)$ indicates the conditional probability that a HB remains intact at time t, given it was intact at time $t=0$. $c(t)$ does not consider breaking of HB at intermittent times between time zero and t. In Fig. 5, we show that $c(t)$ exhibits a stretched exponential behavior followed by a power-law tail [$c(t)\propto t^{-\beta}$, for large t]. In bulk water, a recent study has shown that the exponent β of the tail depends on a dimensionality d of the system, $\beta=d/2$ [34]. Our results show the same results as in Ref. [34] for bulk water. For bulk water, the value of β is around 1.38, which is close to 3/2 at the asymptotically long time. For water confined in a quasi-two-dimensional nanopore slit, the value of β is around 1.02, which is $\sim$2/2. Therefore, our results show that the slow HB dynamics is closely related to the diffusive motion of water, as Luzar and Chandler suggested in Ref. [10].

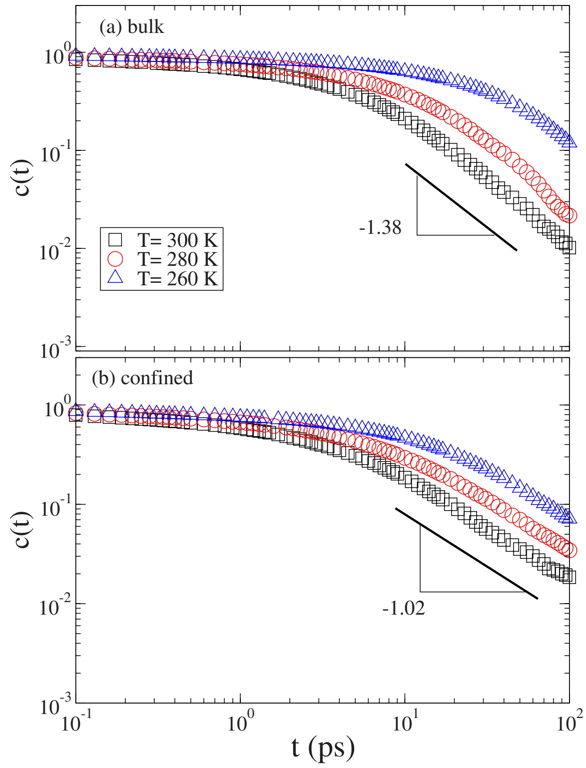

FIG. 5. (Color online) Shown in a log-log plot are the HB autocorrelation functions $c(t)$ for (a) bulk and (b) confined water. In a short-time regime, $c(t)$ shows a stretched exponential behavior. In an asymptotic limit, $c(t)$ exhibits a power-law behavior [$c(t)\propto t^{-\beta}$]. The exponent β of the tail depends on the dimensionality d of the system ($\beta=d/2$). For bulk ($d=3$), the value of β is around 1.38, which is close to 1.5 at the asymptotically long time. For water confined in a quasi- two-dimensional nanopore slit ($d=2$), the value of β is around 1.02.

We define τ_R as the time required for $c(t)$ to decay by a factor of e [10,12]. Unlike τ_{HB}, τ_R represents *slow* motion of HB related to the diffusive motion of water [12]. In Fig. 6, we show τ_R as a function of temperature. Note that τ_R is located in a time scale in which $c(t)$ does not enter the asymptotic power-law tail region yet in Fig. 5. We find that τ_R in confined water is smaller than in bulk water at the same temperature. For bulk TIP5P water, a rapid increase in τ_R as temperature decreases has been reported, which was assigned to the stable environment at lower temperatures [15]. In confined water, the rapid increase in τ_R as temperature decreases is observed in the same pattern as in bulk. The magnitude of τ_R in bulk water from 300 to 260 K is the same as in confined water but shifted by 10 K. For temperatures below 260 K, the two plots are not simply shifted by 10 K, since τ_R in bulk water at temperatures below 260 K increases dramatically. Overall, the temperature response of τ_R in confined water is slower than in bulk water. This decrease in τ_R in confined water indicates that water is less stable in hydrophobic environments than in bulk, as shown in τ_{HB} and the PDF of lifetime.

In Fig. 7, we confirm that the temperature dependence of

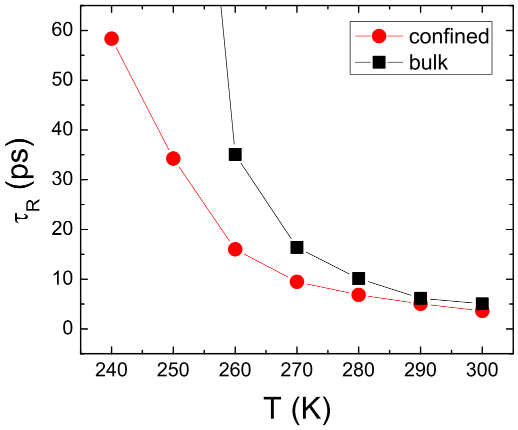

FIG. 6. (Color online) The HB relaxation time τ_R as a function of temperature. Note that τ_R in confined water is smaller than in bulk water. As temperature decreases, τ_R rapidly increases for both confined and bulk water. The temperature response of τ_R in confined water is less pronounced than in bulk water.

τ_R follows a power law [12], and can be fitted by

$$\tau_R \sim (T - T_C)^{-\gamma}, \tag{3}$$

in contrast to the Arrhenius temperature dependence of τ_{HB} (see Figs. 4 and 7). T_C for bulk water is $\simeq 235$ K, which is larger than $T_C \simeq 215$ K for the hydrophobically confined water. However, the exponents γ for both cases are similar ($\gamma \simeq 2.18$ for bulk water and $\gamma \simeq 2.29$ for confined water). This power-law temperature dependence indicates that the dynamics is consistent with the predictions of the mode-coupling theory, suggesting that the slow dynamics of HB may be explained in the same framework as standard transport theory [12,17].

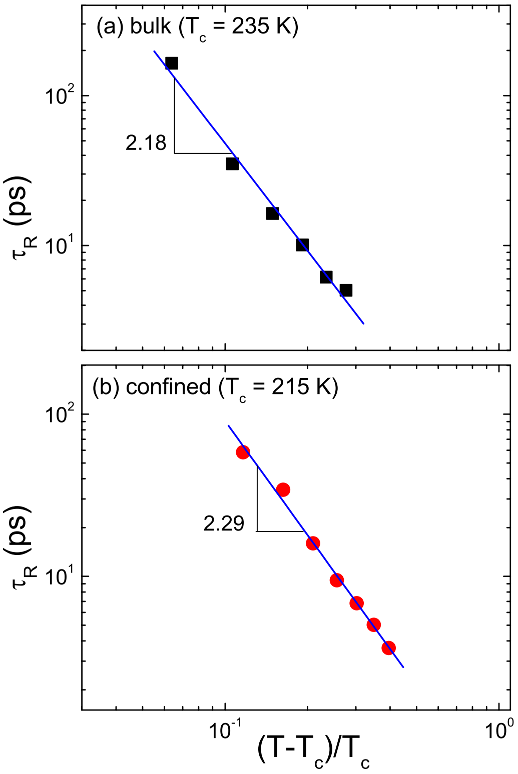

FIG. 7. (Color online) Shown in a log-log plot is the HB relaxation time τ_R as a function of $(T - T_C)/T_C$. τ_R follows a power-law behavior, $\tau_R \sim (T - T_C)^{-\gamma}$. T_C for confined water ($\simeq 215$ K) is different from for bulk water ($\simeq 235$ K), but the exponents for bulk ($\gamma \simeq 2.18$) and confined water ($\gamma \simeq 2.29$) are similar.

In summary, we have investigated HB dynamics by performing MD simulations of TIP5P water confined in a two-dimensional hydrophobic nanopore slit. In our simulations, we found that confined water preserves the characteristics of HB dynamics in bulk water, such as a nonexponential behavior followed by an exponential tail of HB lifetime probability distributions and an Arrhenius temperature dependence of the average HB lifetime. The average number and lifetime of HBs decrease in confined water compared to bulk water at the same temperature. This reduction may be the origin of the reasons for different physical properties of confined water from bulk water, such as the 40 K temperature shift [18,19,32]. The HB autocorrelation function exhibits a stretched exponential behavior followed by a power-law tail with an exponent that depends on the system dimensionality. We also found that the relaxation time in confined water is smaller than in bulk water, indicating that hydrophobic confinement induces a less stable environment for water.

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