PHYSICAL REVIEW E **77**, 030201(R) (2008)

Absence of a diffusion anomaly of water in the direction perpendicular to hydrophobic nanoconfining walls

Sungho Han,[1] Pradeep Kumar,[1,2] and H. Eugene Stanley[1]
[1]*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215, USA*
[2]*Center for Studies in Physics and Biology, The Rockefeller University, New York, New York 10021, USA*

(Received 30 November 2007; published 10 March 2008)

We perform molecular dynamics simulations to investigate the diffusive motion of TIP5P (the transferable intermolecular potential with five points) water in the direction perpendicular to the two hydrophobic confining walls. To calculate the diffusion constant, we use the concept of the characteristic residence time which is calculated from the exponential decay of the residence time probability density function. We find that a diffusion anomaly, increase of diffusion upon compression, is absent in the direction perpendicular to the confining walls down to the lowest temperature we simulate, 220 K, whereas there is a diffusion anomaly, similar to that in bulk water, in the direction parallel to the walls. The absence of a diffusion anomaly in the direction perpendicular to the walls may arise mainly due to nanoconfinement, rather than due to the hydrophobic property of the confining walls. In addition, we find that the temperature dependence of the diffusion constant along the constant density path in the perpendicular direction shows a Vogel-Fulcher-Tammann form.

DOI: 10.1103/PhysRevE.77.030201 PACS number(s): 66.10.C−, 61.20.Ja

In addition to the thermodynamic anomalies of water [1,2], there are the salient dynamic anomalies. For example, in contrast to simple liquids, where the diffusion constant D decreases upon compression, for water at low temperature D first increases upon compression until reaching a maximum and then decreases upon further increase of pressure [3–5].

Confined water shows many structural and dynamic properties different from bulk water due to the geometry of confinement and the interaction with the confining walls [6–19]. Studies of water confined between two hydrophobic plates suggest that the diffusion constant $D_{\parallel}$ along the direction *parallel* to the plates displays a diffusion anomaly, which is the existence of a maximum of $D_{\parallel}$ as a function of a density at constant temperature, similar to bulk water [16]. Moreover, the temperature below which the anomalous diffusive behavior occurs is shifted to lower temperature by about 40 K compared to bulk water [16].

Dynamics in the direction *perpendicular* to the confining plates is modified by the small distance between plates ($L_z \sim 1$ nm). Studies have been carried out to investigate the diffusive motion in the confining direction for many confined systems [20–23]. Liu *et al.* showed that a different treatment for the diffusion constant is needed in the confining direction and used a "dual simulation method" to calculate the more precise diffusion constant at a liquid-vapor interface [20]. Previous studies pointed out two different time regimes (100 ps and 1 ns) of the mean square displacements (MSD) for the complete description of diffusion in confined water and showed a nonlinear MSD due to both spatial inhomogeneity and confinement [21]. The diffusion constant $D_{\perp}$ in the direction perpendicular to the walls is difficult to calculate precisely in nanoconfined water due to the finite and very small space available for water molecules. Before reaching the diffusive regime at which MSD is linearly proportional to time, MSD already enters the plateau regime due to displacement bounded by a finite nanosize space. Hence $D_{\perp}$ cannot be extracted from the MSD. The Green-Kubo relation for $D_{\perp}$ is also not valid for the confined system, as mentioned in Ref. [20].

Here we propose an alternative approach to calculate $D_{\perp}$ and ask whether the diffusion anomaly of water, which has been shown to exist in the parallel direction [16] and in bulk dynamics [1], also exists in the direction perpendicular to the hydrophobic confining plates.

We perform molecular dynamics (MD) simulations of N_W=512 TIP5P (the transferable intermolecular potential with five points) [24] water molecules confined between two infinite parallel smooth plates, separated by L_z=1.1 nm, which are able to contain 2–3 layers of water molecules. The plates are located at the positions $z = \pm 0.55$ nm. We model the water-wall interaction by a 9-3 Lennard-Jones (LJ) potential which is commonly used to represent the effective interaction of water molecules with the confining plates [25,26]. We choose the parameters for the confining potential to have the hydrophobic property, as in Ref. [16]. We perform MD simulations (see Ref. [16] for details) for seven temperatures, T=220, 230, 240, 250, 260, 280, and 300 K, and for eight densities, ρ=0.80, 0.88, 0.95, 1.02, 1.10, 1.17, 1.25, and 1.32 g/cm^3. These densities are calculated by considering the accessible space between the walls, as explained in Ref. [16]. Periodic boundary conditions are used in the x and y directions.

To calculate $D_{\perp}$, we first divide the system into three residence regions along z direction such that there are two symmetric adjacent regions to the surface and one middle region (see Fig. 1). The width of each region is 0.14 nm, and the separation between two adjacent regions is R_z=0.28 nm, which is the same as the average distance between two water molecules. Then, we calculate the residence time PDF $P(\tau_R)$ of water molecules in the given residence region. The residence time τ_R is defined as the time over which water molecules stay in one region before leaving it.

In Fig. 2, we show that $P(\tau_R)$ of the hydrophobic confined water decays exponentially for all temperatures investigated [27]. We calculate the characteristic residence time τ_R^{ch} by finding the inverse slope of a straight line fit to $P(\tau_R)$ on the semilog plot

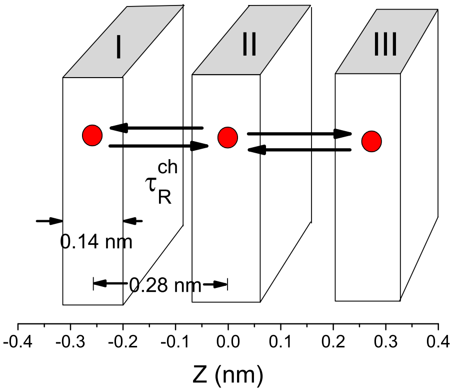

FIG. 1. (Color online) Schematic description of the motion of water molecules in confined space with three defined residence regions. Two confining walls are located at $z=\pm 0.55$ nm. The red circle represents a water molecule. We define the size of one residence region as 0.14 nm and the separation between two regions as 0.28 nm. τ_R^{ch} denotes the characteristic residence time calculated from the residence time distribution. On average, water molecules diffuse the distance of the separation between regions, $R_z = 0.28$ nm, in the z direction perpendicular to the confining walls during a time τ_R^{ch}.

$$P(\tau_R) \sim \exp\left(-\frac{\tau_R}{\tau_R^{ch}}\right). \quad (1)$$

On average, during the time τ_R^{ch} water molecules diffuse the same distance as the separation of two of the defined regions shown in Fig. 1. Using the continuous time random walk formalism and assuming the exponential distribution of waiting times in the long time limit and a Gaussian distribution of step sizes, one recovers the normal Fickian diffusion and the space-time distribution of the diffusive particle is Gaussian. In other words, we can use the first-passage time method to obtain the exponential residence time distribution [28]. When we consider one outer residence region (I or III), the motion of water molecules in the region can be described as a random walk of $N+1$ sites with one absorbing boundary at site 0 and one reflecting boundary at site N. The coupled rate equations with rates toward site 0, T_i, and rates toward site N, R_i, are $\dot{p}_0(t)=T_1p_1(t)$ (at absorbing boundary), $\dot{p}_1(t)=T_2p_2(t)-(T_1+R_1)p_1(t)$, $\dot{p}_i(t)=T_{i+1}p_{i+1}(t)+R_{i-1}p_{i-1}(t)-(T_i+R_i)p_i(t)$ (for $1<i<N$), $\dot{p}_N(t)=R_{N-1}p_{N-1}(t)-T_Np_N(t)$ (at reflecting boundary). In a matrix representation, the above set can be described as $\dot{M}(t)=BM(t)$. Here M is a survival probability vector and B is a matrix whose elements are T_i and R_i. τ_R^{ch} is related to matrix B, $\tau_R^{ch}(n)=-\Sigma_{m=1}^{N}B^{-1}(m,n)$, where $B^{-1}(m,n)$ is (m,n) element of B^{-1} and n,m are the initial and final sites, respectively (see Ref. [28] for the detailed description). Therefore, assuming continuous-time Markov process, $P(\tau_R)$ shows an exponential behavior $[\sim\exp(-\tau_R/\tau_R^{ch})]$.

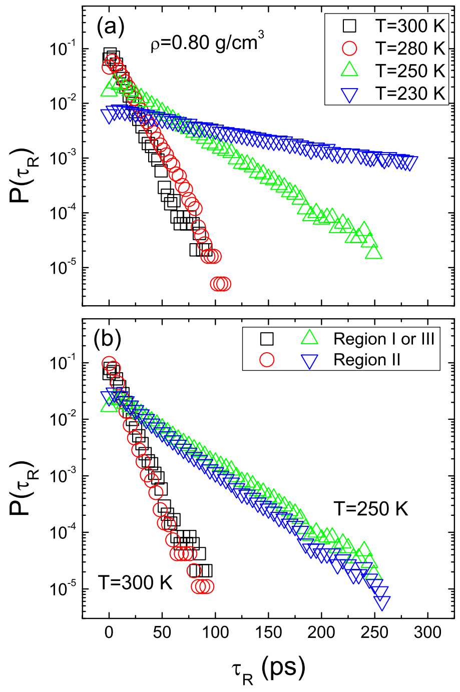

FIG. 2. (Color online) Test of exponential decay of residence time PDF $P(\tau_R)\sim\exp(-\tau_R/\tau_R^{ch})$ for all temperatures and densities investigated. (a) A semilog plot of $P(\tau_R)$ of TIP5P water molecules at different temperatures and fixed density $\rho=0.80$ g/cm^3. (b) $P(\tau_R)$ for different residence regions (see Fig. 1) at $\rho=0.80$ g/cm^3 and $T=250$ and 300 K.

Since water molecules, on average, diffuse the distance equal to the separation between two regions in the time interval τ_R^{ch}, we can write down the diffusion constant $D_\perp$ in the direction perpendicular to the walls

$$D_\perp = \frac{\langle R_z^2\rangle}{2\langle\tau_R^{ch}\rangle}, \quad (2)$$

where $\langle R_z\rangle$ denotes the separation between two residence regions, and $\langle\tau_R^{ch}\rangle$ is the characteristic residence time averaged over an ensemble. To obtain the average value of $D_\perp$, we use the characteristic residence times averaged over three different residence regions. As shown in Fig. 2(b), $P(\tau_R)$ has the same exponentially decaying behavior in different residence regions for all temperatures and densities investigated.

Since the calculation of $D_\parallel$ is possible from the Einstein relation [29], we investigate the validity of Eq. (2) by calculating $D_\parallel$ using both the Einstein relation and the characteristic residence time. In Fig. 3, we show $D_\parallel$ as a function of density for $T=240$ K calculated from both methods for a comparison. We find that the method using the characteristic residence time gives slightly larger value of $D_\parallel$ than using MSD, as shown in Fig. 3. Both methods for $D_\parallel$ in our simulations exhibit a diffusion anomaly with a maximum at $\rho = 1.02$ g/cm^3 as a function of density, the same as in Ref. [16]. Therefore, we can say that Eq. (2) gives the correct value of D and can be used for the calculation of $D_\perp$ to investigate the existence of a diffusion anomaly in the perpendicular direction.

In Fig. 4, we show $D_\perp$ as a function of density for all temperatures studied. $D_\perp$ decreases as the density increases. Contrary to the diffusion anomaly found in the parallel direction (similar to bulk water), as shown in Fig. 3, our results show a diffusion anomaly in the perpendicular direction does

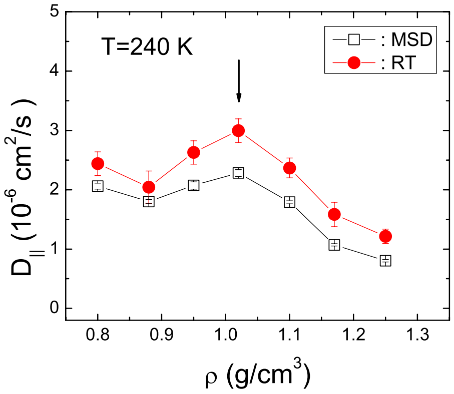

FIG. 3. (Color online) Diffusion anomaly as a function of density for the diffusion constant $D_{\parallel}$ in the direction parallel to the confining walls. $D_{\parallel}$ is calculated by using both the mean square displacement (MSD) predicted by the Einstein relation and the charateristic residence time (RT) at $T=240$ K. Both calculations exhibit a diffusion anomaly in $D_{\parallel}$ as a function of density with a maximum at $\rho=1.02$ g/cm^3.

not exist down to the lowest temperature we simulated. As a result, we conclude that a diffusion anomaly of water is absent in the confining direction down to very low temperatures in nanoconfinement. From the fact that a diffusion anomaly exists in the parallel direction but not in the perpendicular direction, the main contribution to the absence of a diffusion anomaly in the perpendicular direction might be the nanoconfinement rather than the hydrophobic property of the confining walls.

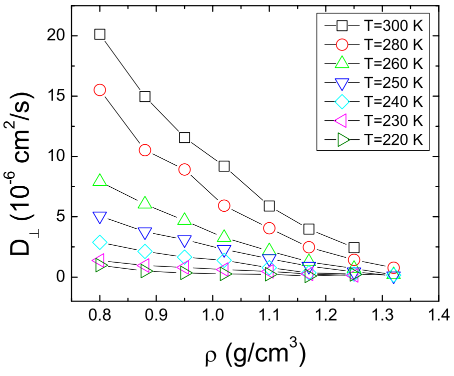

FIG. 4. (Color online) Diffusion constant in the perpendicular direction $D_{\perp}$ as a function of density along constant temperature paths. We find $D_{\perp}$ decreases as density increases over the entire temperature range investigated, suggesting that there is no diffusion anomaly along the perpendicular direction, even at the lowest temperature $T=220$ K simulated. By contrast, for $D_{\parallel}$, there is a diffusion anomaly for $T<250$ K (see Fig. 3 for $T=240$ K).

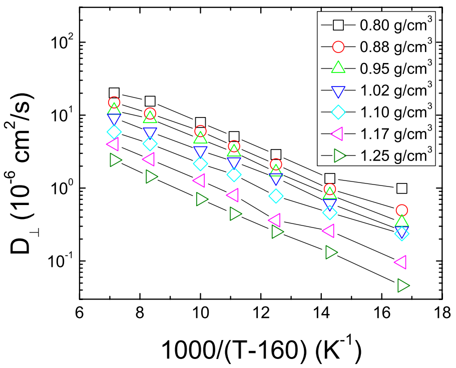

FIG. 5. (Color online) Test of the Vogel-Fulcher-Tammann (VFT) form for $D_{\perp}$. Shown is a semilog plot of $D_{\perp}$ as a function of $1/(T-T_0)$ along seven constant density paths, using the same parameter value $T_0=160$ K.

Next we study $D_{\perp}$ as a function of temperature along a constant density path. In Fig. 5, we find the temperature dependence of $D_{\perp}$ can be fit with a Vogel-Fulcher-Tammann (VFT) form for all the densities studied,

$$D_{\perp} = D_{\perp}^{0} \exp\left(-\frac{A}{T-T_0}\right). \tag{3}$$

Here $D_{\perp}^{0}$, A, and T_0 are fitting parameters, and we use 160 K as the value of the parameter T_0. It has been experimentally observed that there is a fragile-to-strong transition near $T=220$ K in both supercooled water confined in micellar templated mesoporous silica matrices MCM-41 [30] and DNA and protein hydration water [31], which is shown to be connected to a liquid-liquid phase transition scenario [32–37]. In computer simulations of TIP5P hydration water at atmospheric presseure, this non-Arrhenius to Arrhenius crossover occurs at $T\approx 250$ K, the temperature at which the isobaric specific heat has a maximum [35,36]. In contrast to simulation results of TIP5P bulk water, we find that in the confining direction the TIP5P water confined between two hydrophobic plates does not show a non-Arrhenius to Arrhenius dynamic crossover down to the lowest temperature we simulated, $T=220$ K, suggesting that if there is a crossover in the dynamics it would occur at much lower temperature compared to bulk water. This finding is consistent with the temperature shift found for thermodynamic and dynamic properties of water confined between hydrophobic surfaces [16,38].

In summary, we have performed MD simulations of TIP5P water to calculate and investigate the self-diffusion constant in the direction perpendicular to the hydrophobic confining walls. We calculated the diffusion constant using a form similar to the Einstein relation of self-diffusion, described with the separation between two residence regions and the characteristic residence time found from the exponentially decaying residence time distribution. Our simulation results show that a diffusion anomaly does not exist in the direction perpendicular to the confining walls, contrary to the diffusive dynamics of bulk water and the dynamics of confined water in the parallel direction. As the density increases at constant temperature, the diffusion constant continues to decrease without reaching a maximum over the whole temperature range investigated. By comparing the perpendicular direction to the parallel direction, it is reasonable to conclude that this absence of a diffusion anomaly may arise due to nanoconfinement rather than the hydrophobic property of the confining walls. Since bulk water displays a diffusion anomaly, one expects that if $L_z \gg 1$ nm, the diffusion anomaly in the perpendicular direction will be restored. We are planning to carry out in the future an investigation of an approach to the bulk limit. In addition, we find that the temperature dependence of the diffusion constant along the constant density path in the perpendicular direction shows a VFT form.

We thank C. A. Angell, J. A. Brunelle, S. V. Buldyrev, W.-S. Jung, J. Kim, J. Luo, M. G. Mazza, S. Sastry, K. Stokely, E. Strekalova, L. Xu, and Z. Yan for the helpful discussions, and NSF Grant No. CHE0606489 for support.

[1] P. G. Debenedetti, J. Phys.: Condens. Matter **15**, R1669 (2003); P. G. Debenedetti and H. E. Stanley, Phys. Today **56**, 40 (2003).

[2] C. A. Angell, Annu. Rev. Phys. Chem. **34**, 593 (1983); in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1982), Vol. 7.

[3] H. E. Stanley and J. Teixeira, J. Chem. Phys. **73**, 3404 (1980).

[4] F. X. Prielmeier, E. W. Lang, R. J. Speedy, and H.-D. Lüdemann, Phys. Rev. Lett. **59**, 1128 (1987); Ber. Bunsenges. Phys. Chem. **92**, 1111 (1988).

[5] C. A. Angell, E. D. Finch, L. A. Woolf, and P. Bach, J. Chem. Phys. **65**, 3063 (1976).

[6] K. Koga, X. C. Zeng, and H. Tanaka, Phys. Rev. Lett. **79**, 5262 (1997).

[7] K. Moroshige and K. Kawano, J. Chem. Phys. **110**, 4867 (1999).

[8] J. Slovák, K. Koga, H. Tanaka, and X. C. Zeng, Phys. Rev. E **60**, 5833 (1999).

[9] K. Koga, H. Tanaka, and X. C. Zeng, Nature (London) **408**, 564 (2000).

[10] P. Gallo, M. Rovere, and E. Spohr, Phys. Rev. Lett. **85**, 4317 (2000); J. Chem. Phys. **113**, 11324 (2000); **116**, 342 (2002).

[11] R. Bergman and J. Swenson, Nature (London) **403**, 283 (2000).

[12] J. Slovák, H. Tanaka, K. Koga, and X. C. Zeng, Physica A **319**, 163 (2003).

[13] R. Zangi and A. E. Mark, Phys. Rev. Lett. **91**, 025502 (2003); J. Chem. Phys. **119**, 1694 (2003); **120**, 7123 (2004).

[14] R. Zangi, J. Phys.: Condens. Matter **16**, S5371 (2004).

[15] K. Koga and H. Tanaka, J. Chem. Phys. **122**, 104711 (2005).

[16] P. Kumar, S. V. Buldyrev, F. W. Starr, N. Giovambattista, and H. E. Stanley, Phys. Rev. E **72**, 051503 (2005).

[17] N. Giovambattista, P. J. Rossky, and P. G. Debenedetti, Phys. Rev. E **73**, 041604 (2006).

[18] P. Kumar, F. W. Starr, S. V. Buldyrev, and H. E. Stanley, Phys. Rev. E **75**, 011202 (2007).

[19] I. Brovchenko and A. Oleinikova, J. Chem. Phys. **126**, 214701 (2007).

[20] P. Liu, E. Harder, and B. J. Berne, J. Phys. Chem. B **108**, 6595 (2004).

[21] M. Sega, R. Vallauri, and S. Melchionna, Phys. Rev. E **72**, 041201 (2005); P. Gallo and M. Rovere, *ibid.* **76**, 061202 (2007).

[22] B. Lin, J. Yu, and S. A. Rice, Phys. Rev. E **62**, 3909 (2000).

[23] T. Benesch, S. Yiacoumi, and C. Tsouris, Phys. Rev. E **68**, 021401 (2003).

[24] M. W. Mahoney and W. L. Jorgensen, J. Chem. Phys. **112**, 8910 (2000); M. Yamada, S. Mossa, H. E. Stanley, and F. Sciortino, Phys. Rev. Lett. **88**, 195701 (2002).

[25] W. A. Steele, *The Interaction of Gases with Solid Surfaces* (Oxford, New York, 1974).

[26] J.-P. Hansen and I. P. McDonald, *The Theory of Simple Liquids* (Academic, London, 2006).

[27] The anomalous dynamics becomes subdiffusive when water is confined in Vycor pores with the condition of low hydration [P. Gallo and M. Rovere, J. Phys.: Condens. Matter **15**, 7625 (2003)]. This subdiffusive motion is related to a power law behavior of $P(\tau_R)$. However, our results show that in hydrophobic confinement, $P(\tau_R)$ has an exponential behavior for all temperatures and densities investigated.

[28] A. Bar-Haim and J. Klafter, J. Chem. Phys. **109**, 5187 (1998).

[29] D. C. Rapaport, *The Art of Molecular Dynamics Simulation* (Cambridge University Press, Cambridge, UK, 2004).

[30] L. Liu, S.-H. Chen, A. Faraone, C.-W. Yen, and C.-Y. Mou, Phys. Rev. Lett. **95**, 117802 (2005).

[31] S.-H. Chen, L. Liu, X. Chu, Y. Zhang, E. Fratini, P. Baglioni, A. Faraone, and E. Mamontov, J. Chem. Phys. **125**, 171103 (2006).

[32] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature (London) **360**, 324 (1992).

[33] O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).

[34] I. Brovchenko, A. Geiger, and A. Oleinikova, J. Chem. Phys. **118**, 9473 (2003).

[35] L. Xu, P. Kumar, S. V. Buldyrev, S.-H. Chen, F. Sciortino, P. H. Poole, and H. E. Stanley, Proc. Natl. Acad. Sci. U.S.A. **102**, 16558 (2005); P. Kumar, S. V. Buldyrev, S. L. Becker, P. H. Poole, F. W. Starr, and H. E. Stanley, *ibid.* **104**, 9575 (2007).

[36] P. Kumar, Z. Yan, L. Xu, M. G. Mazza, S. V. Buldyrev, S.-H. Chen, S. Sastry, and H. E. Stanley, Phys. Rev. Lett. **97**, 177802 (2006).

[37] D. Paschek, Phys. Rev. Lett. **94**, 217802 (2005).

[38] X.-Q. Chu, A. I. Kolesnikov, A. P. Moravsky, V. Garcia-Sakai, and S.-H. Chen, Phys. Rev. E **76**, 021505 (2007).