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Dynamics and Energetics of Hydrophobically Confined Water

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Keywords

HYDROPHOBIC EFFECT; POLARIZABILITY; HYDROPHOBIC CONFINEMENT; DIFFUSION; WETTING; DEWETTING; DYNAMICS

I. INTRODUCTION

Water plays an important role in mediating molecular scale processes such as aggregation/assembly, pocket-ligand binding, and polymer/peptide folding.(REF) These processes are largely driven by hydrophobic effects, which work to minimize disruption of water-water interactions by nonpolar solutes or surfaces. In systems in which multiple large-scale hydrophobes (radius of curvature on the order of 1 nm or larger) are solvated, water can become hydrophobically confined. Water under hydrophobic confinement has been shown to demonstrate properties unique from those of bulk water such as XXX,XXX,XXX. Such wetting/dewetting transitions have important implications for XXX.

Hydrophobic confinement has been studied using molecular dynamics simulations using a variety of model systems. Pioneering work by Hummer and coworkers investigated the flow of confined water through carbon nanotubes and observed transduction occurring in “pulses.”?

Yu and Rick studied the thermodynamics of water confined in regions model protein pocket enclosures in which the solvent accessible volume, hydrophobicity, and treatment of electrostatics (fixed-charge versus polarizable representations).¹ Studies by Setny and coworkers have considered the behavior of water in model pocket-ligand systems. Results Investigations employing solvated hydrophobic surface plates have also provided physical insights to the role of water in mediating hydrophobic assembly and the dynamic nature of confined water.²⁻⁵

Water confined between two large-scale hydrophobic surfaces exhibits interesting behavior that is dependent on the distance in which the surfaces are separated. At low distances (although still large enough to accommodate a layer of water molecules), an unoccupied interior region is observed and energetically favored. Conversely, at large separation distances the confined interior region becomes wet. At some intermediate distance (which we will denote the critical distance, d_c) Such observations are common to numerous studies

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using various water and hydrophobic surface models^{2–5} and are predicted based on capillary theory.

In Figure 1 we illustrate the time profiles for number of water molecules residing in the confined region as a function of the distance between two model hydrophobic plates for several common water models as studied in Ref 5. Near the critical distance, the interior region undergoes rapid wetting/dewetting transitions. The probability of finding the interior either filled or unfilled will then be equal at the critical distance, while the probability of a unfilled interior will be higher/lower than a filled interior for distances less than/greater than the critical distance (respectively). The critical plate-separation distance is also interesting from the hydrophobic assembly standpoint, since this distance coincides with the position of a barrier in the potential of mean force which opposes hydrophobic assembly (see Figure 2). This is intuitive since a dewetting process will be a prerequisite for direct contact between plates. Furthermore, simulations by Huang, Margulis, and Berne demonstrated that the rate at which hydrophobic ellipsoids approach each other is over three times faster once the region separating the hydrophobes becomes “dewetted”.⁶ We note that the polarizable TIP4P-FQ model uniquely shows no barrier opposing hydrophobic assembly.

In this contribution, we complement our previous study of hydrophobic assembly⁵ with a particular focus on the dynamics of water under hydrophobic confinement and the energetics of wetting/dewetting processes. Through such analyses we seek to further understand differences in hydrophobic assembly and confinement for different water models. We outline our computational methodology and protocol in Section II. In Section III, we present our results regarding wetting/dewetting energetics (Section III A) and dynamics (Section III B). We conclude our study in Section ?? with a summary of our results and general discussion.

II. METHODS

Molecular dynamics simulations were performed in the canonical ensemble (*NVT*) using the CHARMM molecular modeling program⁷. We use the system from our previous work⁵ which consisted of two hydrophobic plates hydrated with 4538 water molecules in a $36 \text{ \AA} \times 36 \text{ \AA} \times 200 \text{ \AA}$ box. Two liquid-vapor (LV) interfaces were present in the *z*-direction with at least $25 \text{ \AA}$ of bulk water phase separating the LV interfaces from the water-plate (WP) interfaces. Water molecules were represented by each the TIP3P (modified for CHARMM),⁸ (REF) TIP4P,⁸ SPC/E,⁹ TIP4P-FQ,¹⁰ SWM4-NDP¹¹ models, the latter two are polarizable models. Each plate consisted of 31 atoms arranged in a triangular lattice with bond length of $3.2 \text{ \AA}$. The interplate interactions were modeled via a “12-6” Lennard-Jones potential with parameters of $R_{\min} = 4.4898 \text{ \AA}$ and $\epsilon = 0.1195 \text{ kcal/mol}$ centered on each atom; intraplate interactions were set to zero.^{2,5} The plates were held in registry with respect to each other and the positions of all plate atoms were held fixed throughout the course of the simulation for each sampled distance in the range $d = 3.6 \text{ \AA}$ to $d = 14.4 \text{ \AA}$. We sample approximately thirty distances for each model. Each distance was sampled using 5–10 replicates, resulting in at least XX ns per window. Sampling was increased to at least XX ns near the critical point in order to thoroughly sample wetting/dewetting transitions. Interactions between plates and water were fixed to reproduce the combined interaction of SPC/E water and the

plates ($R_{min} = 4.022 \text{ \AA}$ and $\varepsilon = 0.1362 \text{ kcal/mol}$), as used in previous work.⁵ Parameters used to model water-water, water-plate, and plate-plate interactions are summarized in Table 1 of Ref⁵. We refer the reader to Ref⁵ for the functional forms of these interactions.

Long-range electrostatic contributions were treated using particle-mesh Ewald (PME)¹² with approximately $1 \text{ \AA}$ fft grid spacing and a screening parameter $\kappa = 0.330$. Nonbonded interactions were gradually truncated to zero from 11 to $12 \text{ \AA}$. Simulation temperature was maintained at 300 K using a Nosé-Hoover thermostat. The rigid molecular geometry of each water molecule was maintained using SHAKE.¹³ For simulations involving TIP4P-FQ water, fictitious charge degrees of freedom were assigned masses of $0.000069 \text{ kcal/(mol ps}^2\text{)}$. These charge degrees of freedom were coupled to a thermostat at 1 K with a mass of $0.005 \text{ kcal/(mol ps}^2\text{)}$ using the Nosé-Hoover¹⁴ method. The classical equations of motion for TIP4P-FQ, TIP4P, SPC/E, and TIP3P were propagated using the Verlet leapfrog integrator; SWM4-NDP was propagated using the Velocity-Verlet integrator. Time steps of 1.0 fs were used SPC/E, TIP3P, TIP4P, and SWM4-NDP, while a 0.5 fs time step was used for a TIP4P-FQ.

III. RESULTS

A. Energetics of Wetting/Dewetting

As mentioned in the Introduction and depicted in Figure 1, spontaneous transitions between an unfilled and filled interior plate region occur at separation distances near some critical distance, d_c . From the distributions of the number of water molecules confined between the plates at a given separation distance over the course of the trajectory, the probability of finding N molecules between the plates (separated by a distance d) can be calculated for each of the water models. At low distances, unfilled (low N) states are probable, whereas filled (high N) states are probable at large distances. Near the critical plate-separation distance both filled and unfilled states are probable. From the probability profiles of finding N water molecules in a cylindrical sampling volume between the plates (depicted in the right panels of Figure ??), we can calculate the relative free energies for filled and unfilled states as:

$$\Omega(N, d) = -RT \ln \left(\frac{P(N, d)}{P(N_0, d)} \right) \quad (1)$$

where Ω represents the free energy associated with having N water molecules between the plates at a separation distance d , P is the corresponding probability, and $P_0(N_0)$ is the reference probability. We choose N_0 to be the number of water molecules in the most favorable unfilled state (where the probability of a low density state is maximized). Results of these free energy calculations are shown in Figure 3. Profiles for each water model demonstrate the same qualitative behavior. At low separation distances ($d < d_c$) the unfilled state is energetically favorable; filled states are favored at larger separation distances ($d > d_c$). The observed minima for the filled and unfilled states are separated by an energetic barrier which opposes wetting/dewetting transitions. In order to assess the specific features of these profiles, we consider variation of barrier heights and the energetic difference between filled and unfilled states in Figure 4. For these profiles, barrier height is defined as the difference between the local maximum separating the two states and the minimum

corresponding to the specified state. Furthermore, since the critical distances are not the same for all models studied, we choose to present these profiles as function of distance from the critical distance ($d-d_c$) such that 0 corresponds to the critical distance. Figure 4a depicts the variation of the barrier height associated with wetting process. Expectedly, the barrier for wetting decreases with increasing separation distance; however, a barrier is still present even for distances in which the filled state is most energetically stable. Conversely, the barrier heights for the dewetting process (Figure 4b) are shown to increase with increasing distance. Finally, Figure 4c shows the free energy of the filled state relative to the unfilled state ($\Omega_{u \rightarrow f} = \Omega_f - \Omega_u$). Over the range of distances showing oscillations between filled and unfilled states, this profile is relatively linear. We include the linear fit for each model's profile as a dashed/dotted line. The x -intercept of this fit (using the original, unshifted data) represents the critical distance. We define the critical distance (as used in this study and for the shifting of these profiles) as the point in which $\Omega_f = \Omega_u$, based on the linear fits. This is in principle similar to the probability based definition used in our previous work. As a result, we calculate critical distances of $d_c = 10.45, 10.0, 9.8, 9.8, 9.9 \text{ \AA}$ for TIP4P-FQ, SWM4-NDP, SPC/E, TIP3P, and TIP4P, respectively. These are all in excellent agreement (within $0.1 \text{ \AA}$) with our previous estimates;⁵ slight differences can be attributed to increased sampling and errors due to linear regression analysis.

While the above analysis gives information pertaining to the relative stability of a wetted versus dewetted interior regions, information regarding the extent to which water can enter the confined region is lost due to sampling a single static volume. That is, we do not distinguish between molecules that reach the very center of the confined region or only reach as far as the edges of the sampling region. As a result, we consider the potential of mean force for water entering the region between the two plates as a function of the radial distance from the z -axis, which coincides with the vector normal to the center of geometry of the two plates. The use of r as the reaction coordinate for this analysis assumes radial symmetry, although some topological differences may arise due to the geometry of the plates. We calculate this PMF as

$$\Delta W(r) = -RT \ln \left(\frac{\rho(r)}{\rho_{\text{bulk}}(r)} \right) \quad (2)$$

where r represents the radial distance from the z -axis. $\rho(r)$ is the density of water in a cylindrical sampling volume in which a radial bin size of $0.1 \text{ \AA}$ was used in all systems at all separations. The height of the cylinder was taken as $d - 2\sigma_{\text{OP}}$, where $\sigma_{\text{OP}} \approx 3.6$ is the Lennard-Jones radius between a water molecule and plate atom; this effectively limits the sampling to the volume between the plates in which water would not be on the repulsive wall of the LJ potential. We note that simply choosing d for this analysis would artificially reduce the density in the confined region and lead to a larger energetic penalty for entering the interior region. The PMF is relative to bulk region ($r = 17 - 18 \text{ \AA}$ where the water is influenced least by the plates). Profiles are shown in Figure 5 for the models at various separation distances. The profiles for $d = 7.4 \text{ \AA}$ represent the lowest separation sampled in which water could enter the sampling volume. It is unfavorable for water to move from bulk to the interior of the confined region (which we will consider $r < 8.0 \text{ \AA}$ as was used as the

criterion in our previous analyses). The barrier increases sharply as r decreases. This suggests the relative difficulty of a water molecule reaching the center of the confined region; molecules counted as in interior are most commonly located at $r \approx 8 \text{ \AA}$. We note profiles can only be shown where water is sampled; thus “missing” portions of the profile at low r indicate water was not found at these distances throughout the course of the simulation. Similar results are seen for the $d = 8.4 \text{ \AA}$ profiles, although water is able to penetrate further into the confined region at this distance. By $d = 9.6 \text{ \AA}$ significant differences among models are observed; such differences are expected due to the differences in the average number of confined water molecules at these near critical distances. However, beyond the critical region ($d > 11.0 \text{ \AA}$), the interior is consistently filled. Accordingly, there is no energetic penalty for water to move from the bulk to the confined region. It is seen that the PMF is actually reduced in the confined region relative to the bulk, although this difference is quite low (less than 0.1 kcal/mol).

B. Water Dynamics

We compare the diffusion constants for each water model in two different regions: (1) the volume confined by the plates and (2) the bulk water region. For this analysis, we consider the $d = 14.4 \text{ \AA}$ (dissociated) system which allows for the most sampling of confined water. This choice is not arbitrary, however, since near-critical plate separation distances will result in low density that may influence enhanced diffusion. We consider other distances in subsequent analyses. Sampling for diffusion calculations utilized cylindrical volumes defined as follows. For the confined region, molecules within the cylinder of dimensions $r = 8 \text{ \AA}$ and length $|z_{\text{Plate2}} - z_{\text{Plate1}}| = 14.4 \text{ \AA}$ was sampled. The bulk region was sampled using cylinders with the same radius and length as before, however, positioned between the water-plate and water vapor interfaces. In order to increase sampling, both the positive ($z > 0 \text{ \AA}$) and negative ($z < 0 \text{ \AA}$) regions of the system were sampled. Each cylinder was bound by the dimensions $|z| = 17.2$ to $|z| = 31.6 \text{ \AA}$ and $r = \sqrt{x^2 + y^2} = 8 \text{ \AA}$, where the z -position was chosen to minimize the influence of the interfaces on the bulk properties. In addition, to the consideration of the volume we are sampling, the direction of translational diffusion must also be considered. We calculate three diffusion constants for each region of each model as (1) diffusion lateral to the plate-water interface (D_{xy}), (2) diffusion normal to the plate-water interface (D_z), and (3) diffusion in all three dimensions (D). We calculate each as follows¹⁵:

$$D_{xy}[k] = \lim_{t \rightarrow \infty} \frac{1}{4N(k, t)t} \sum_{i, \tau} [x_i(t+\tau) - x_i(\tau)]^2 + [y_i(t+\tau) - y_i(\tau)]^2 \quad (3)$$

$$D_z[k] = \lim_{t \rightarrow \infty} \frac{1}{2N(k, t)t} \sum_{i, \tau} [z_i(t+\tau) - z_i(\tau)]^2 \quad (4)$$

$$D[k] = \lim_{t \rightarrow \infty} \frac{1}{6N(k, t)t} \sum_{i, \tau} [x_i(t+\tau) - x_i(\tau)]^2 + [y_i(t+\tau) - y_i(\tau)]^2 + [z_i(t+\tau) - z_i(\tau)]^2. \quad (5)$$

In the above equations, sum is taken only over all molecules that exist in region k during the time interval $[\tau, \tau + t]$. $N(k, t)$ is the total number of water molecules sampled in region k at a time interval t from the time origin, τ . Each diffusion constant is further normalized by the dimensionality of translation, $2d$, where d is the number of translational degrees of freedom. This approach allows us to treat for multiple time origins in that if a molecule initially outside a given region enters that region at some point during the trajectory, it may contribute to the overall diffusion in that region.

Diffusion constants are given in Table I. In addition to the diffusion constants D_{xy} , D_z , and D in the confined and bulk regions, we calculate the ratio of each diffusion constant in the confined region to the diffusion constant in bulk. This enables us to easily assess whether the diffusion between the plates is enhanced, reduced, or comparable to bulk diffusion. Consistent with values determined from molecular dynamics simulations of pure water, we observe diffusion (considering D) decreases for the models studied as: TIP3P > TIP4P > SPCE > SWM4-NDP > TIP4P-FQ. We note that the models treating polarizability through self-polarization energy corrections (SPC/E, SWM4-NDP, TIP4P-FQ) demonstrate the lowest diffusion constants, in good agreement with experiment. As discussed in our previous work,⁷ the self-polarization correction allows for a more cohesive water-water interaction in the condensed phase and this reduction in diffusion can be viewed a manifestation of this effect. Comparing the diffusion in lateral (D_{xy}) and normal (D_z) directions, the diffusion normal to the plates is consistently slowed down (by approximately $0.2 \times 10^{-5} \text{ cm}^2/\text{s}$) relative to lateral diffusion. This suggests that the presence of the interfaces and neighboring regions of structured/ordered water may still have some influence. Furthermore, since the isotropic diffusion constant is dependent on the contributions in each directions (that is, $D \approx (2D_{xy} + D_z)/3$), it is also reduced relative to the lateral diffusion.

Considering diffusion in the hydrophobically confined region, the discrepancy between D_{xy} and D_z becomes more significant than in the bulk environment. This is expected from the spatial restrictions on diffusion in the z -direction. Interestingly, the extent of relative reduction of D_z in the confined region is quite consistent among all models ($D_z/D_{xy} \approx 0.54 - 0.58$). Again, the reduction in D_z slows down the isotropic diffusion of water in the confined region. Also shown in Table I are the ratios of each diffusion constant in the confined region to the diffusion constant in the bulk. We will first consider D_{xy} which describes the diffusion in the direction that water enters and leaves the confined region or diffusion with the greatest influence on wetting and dewetting. All the models investigated except TIP4P-FQ show near-bulk lateral diffusion in the interior (ranging within a 4% slowdown to a 6% enhancement. TIP4P-FQ, however, shows a significant (26%) enhancement relative to bulk. We offer several explanations for TIP4P-FQ's unique behavior. First, TIP4P-FQ shows the lowest average number of water molecules confined between the plates at $d = 14.4 \text{ \AA}$.⁵ The reduced density in this region (relative to the bulk) facilitates faster diffusion. Furthermore, in our previous work we demonstrated that the average molecular dipole moment of TIP4P-FQ water is slightly reduced relative to the average bulk value of $\mu = 2.62 \text{ D}$ (Figure 7 of Ref 5). This reduction is likely to weaken the intermolecular attractions between confined water molecules. The other polarizable model used in this study, SWM4-NDP, also demonstrated a slightly reduced dipole moment (relative to the bulk value) at $d = 14.4 \text{ \AA}$,

although not to the extent of TIP4P-FQ. Furthermore, SWM4-NDP had more water molecules confined between the plates at $d = 14.4 \text{ \AA}$. These observations are consistent with an enhanced D_{xy} relative to bulk (1.06) for SWM4-NDP that is still considerably lower than that seen for TIP4P-FQ.

In all cases, D_z is reduced between the plates relative to bulk (55–78%). TIP4P-FQ shows the least reduction (78%) which we attribute to the

Specifically, we consider the probability that a water molecule initially residing within the confined region will remain there at time t . For this analysis, we consider molecules that are between the plates at time $t_0 = 0$ and remain between the plates at t with no instances of leaving the confined region. The probability is then

$$P(t) = \frac{1}{N(0)} \sum_{t_0} N(t_0, t) \quad (6)$$

where t_0 denotes consideration of multiple time origins and $t = t_0 + \tau$ is the time a water molecule persists in the confined region after it was initially observed at time origin t_0 . The number of molecules confined at each time t is normalized by the number of molecules observed at $t = 0$, such that $P(0) = 1$. Since we cannot consider transitions occurring on timescales faster than our frequency for saving coordinates, we expect some dependence of this property on the choice of save frequency. However, we employ the same save frequency among models for this analysis, allowing for at least a qualitative comparison between models.

Representative probability profiles for each model (at the largest separation distance $d = 14.4 \text{ \AA}$) are shown in Figure 6a. For distances lower than the critical distance, the profile decays rapidly. The rate of decay decreases as the plate separation distance increases. In order to quantify these results as a function of plate separation distance, probability profiles were fit to a stretched exponential of the form:

$$P(t) = P_0 \exp[-(t/\tau)^\gamma] \quad (7)$$

where P_0 , τ , and γ were adjustable parameters used during the fitting procedure. P_0 is probability that a water molecule initially confined is between the plates at time $t=0$; for the final functional fits, P_0 is approximately 1. γ represents the stretched exponential constant and was generally between 0.60 and 0.85, suggesting deviation from first order decay. τ is characteristic lifetime in which a water molecule resides in the confined region. Figure 6b demonstrates the variation of τ as a function of d for each model. The shape of these profiles are qualitatively similar to those depicting the average number of water molecules between the plates as a function of distance. At low interplate distances the lifetime of water between the plates is short. This may be a consequence of water molecules partially penetrating the interior region. Such partial penetration will occur for all plate separation distances to some extent so it is unlikely this is the primary reason for differences between lifetimes at small and large separation distances. Furthermore, we attempt to minimize this effect through use of a sampling radius of $8 \text{ \AA}$ which limits sampling of “edge” regions where this is most

frequent. At low separation distances the density of the interior region is low (essentially vapor-like). As a result, one would expect the diffusion of molecules in this region to deviate significantly from bulk behavior and become more like water vapor. Previous work by Liu et al¹⁶ suggests that diffusion of water near the liquid-vapor interface is enhanced relative to bulk water due to the increased freedom of mobility in the direction devoid of neighboring water molecules. Certainly, such behavior is also expected here albeit not as pronounced due to confinement effects arising from the plates. Regarding the dependence of water lifetime on plate-separation distance, the form of this profile is quite similar to the distance dependence for the region between the plates (for instance). This further supports the influence the local density has on the diffusion in this confined region. Other factors may influence the general form of this profile, but are expected to have only secondary influence on these results. For instance, the increase in sampling volume with increasing d will give water more freedom in its diffusion within the confined region. Such an effect (in the absence of other factors) would result in a linear increase in the lifetimes with d , which is clearly not the dominant form of this profile. Furthermore, the lifetime profiles demonstrate large uncertainties in the critical distance region ($d \approx 9.4 - 10.6 \text{ \AA}$). This observation can be attributed to the significant fluctuations between filled (high density) and unfilled (low density) interior states, further supporting the influence of confined density on the water lifetime.

The relative ordering of water lifetimes at the largest separation distance is $\tau_{\text{SPC/E}} > \tau_{\text{SWM4-NDP}} > \tau_{\text{TIP4P-FQ}} > \tau_{\text{TIP4P}} > \tau_{\text{TIP3P}}$. This differs from the reverse ordering of bulk diffusion constants where TIP4P-FQ would be expected to have the slowest diffusion constant (and correspondingly the longest lifetime). For the reasons discussed above in the context of diffusion constants, the confined diffusion properties differ significantly from bulk properties. We expect the lifetime of water between the plates to be largely due to translational diffusion of confined water in the direction parallel to the plate-water interface (D_{xy}). Correspondingly, we note that the ordering of water lifetimes matches the ordering for the magnitude of D_{xy} for each model in the confined region.

IV. DISCUSSION AND CONCLUSIONS

One distinguishing characteristic of the TIP4P-FQ model compared to the polarizable SWM4-NDP model is the critical separation distance ($10.45 \text{ \AA}$ versus $9.95 \text{ \AA}$). This enhanced d_c for TIP4P-FQ may have implications for features of the potential of mean force. In particular, TIP4P-FQ uniquely shows no barrier to plate association. From a force balancing perspective, the barrier indicates the forces opposing association is dominant. This can be viewed as interior waters pushing the plates apart with greater force than bulk water pushes the plates together. In the case of subcritical distances ($d < d_c$), the interior is mostly unfilled and the plates can be “pushed” together with minimal resistance (leading to the steep decrease in the PMF). For TIP4P-FQ water, the critical distance is approximately $0.5 \text{ \AA}$ higher than the other models, yet still has the same number of water molecules between the plates at the critical distance. This allows for less resistance to plate association for the TIP4P-FQ at the critical distance, or equivalently, a reduction of the PMF barrier. This relationship between PMF barrier and critical distance is further supported in Figure 7 where we consider these at various distances for the TIP4P-FQ and SWM4-NDP.

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Figure 1.

Representative plots of the wetting and dewetting of the region between the plates near the critical distance for each model (left). For SWM4-NDP, we show results from two independent trajectories: one in which the interior region is initially filled and one in which it is initially empty. Panels in the second column are the probability distributions for finding a given number of molecules between the plates at a given separation distance. Results for separation distances leading to mostly unfilled states, mostly filled states, both filled and unfilled states (critical distance) are shown for each model.

Figure 2.

Potential of mean force for plate association in several common water models. Profiles are shown as a function of separation distance and are relative to the dissociated state. The inset shows the relationship of the position of the PMF barrier and the critical distance for each model (indicated by vertical lines).

Figure 3.

Free energies of filling and unfilling for the models studies at near-critical plate separation distances. All profiles are relative to the unfilled state (local free energy minimum at low N). A dotted horizontal line ($\Omega = 0$ kcal/mol) is shown to easily distinguish which state (unfilled/filled) is energetically favored.

Figure 4.

Free energy barriers for wetting/dewetting transitions and the difference in free energy between filled and unfilled states. (a) Free energy barrier opposing a wetting process. (b) Free energy barrier opposing a dewetting process. (c) Difference in free energy between the filled and unfilled states and linear fits to each. All profiles are shown as a function of distance relative to the critical distance for each model (as determined via the linear fits in panel c).

Figure 5.

Potential of mean force experienced by water entering the hydrophobically confined region for the water models studied. All profiles are shown as a function of the radial distance of a molecule from the z-axis. Various separation distances are shown, spanning distances in which water is initially able to fit in the confined region to separations that are near-bulk.

Figure 6.

Lifetime of water molecules between the plates. (a) The probability that a water molecule initially between the plates will remain there at a given time, t . A representative profile from each model is shown at a plate separation distance of $14.4 \text{ \AA}$. (b) Characteristic lifetime of each model as a function of plate separation distance. This parameter, τ , is based on a stretched exponential fit to probability profiles like those in panel a. Error bars are determined from the standard deviation of this fitted parameter over all replicates at a given distance.

Figure 7.

Temperature dependence on the PMF (barrier) in the critical region for (a) TIP4P-FQ and (b) SWM4-NDP. The variation of critical distance for TIP4P-FQ and SWM4-NDP with temperature. The dependence of the SWM4-NDP barrier height with temperature.

Table I

Diffusion constants calculated with $d = 14.4 \text{ \AA}$. Values in parentheses denote the uncertainty in the last reported digit as determined from the standard deviation of independent trajectories. All values in units of $10^{-5} \text{ cm}^2/\text{s}$.

Model	Bulk			Interior			Interior/Bulk		
	D_{xy}	D_z	D	D_{xy}	D_z	D	D_{xy}	D_z	D
TIP3P	4.79(6)	4.58(10)	4.69(4)	4.63(2)	2.50(4)	3.92(2)	0.97(1)	0.55(1)	0.84(1)
TIP4P	3.43(2)	3.20(4)	3.35(1)	3.52(4)	1.94(2)	2.99(3)	1.04(2)	0.61(1)	0.89(1)
SPC/E	2.62(1)	2.38(2)	2.54(1)	2.52(3)	1.45(3)	2.16(2)	0.96(1)	0.61(1)	0.85(1)
SWM4-NDP	2.47(4)	2.32(1)	2.42(3)	2.62(5)	1.48(4)	2.24(5)	1.06(2)	0.64(2)	0.93(2)
TIP4P-FQ	2.19(3)	1.98(1)	2.12(3)	2.74(6)	1.54(5)	2.34(5)	1.26(4)	0.78(2)	1.11(3)