Electrostatic contribution from solvent in modulating single-walled carbon nanotube association

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(Received 20 June 2014; accepted 28 July 2014; published online 17 September 2014)

We perform all-atom molecular dynamics simulations to compute the potential of mean force (PMF) between two (10,10) single-walled carbon nanotubes solvated in pure nonpolarizable SPC/E and polarizable TIP4P-FQ water, at various temperatures. In general, the reversible work required to bring two nanotubes from a dissociated state (free energy reference) to contact state (free energy minimum) is more favorable and less temperature-dependent in TIP4P-FQ than in SPC/E water models. In contrast, molecular properties and behavior of water such as the spatially-resolved water number density (intertube, intratube, or outer regions), for TIP4P-FQ are more sensitive to temperature than SPC/E. Decomposition of the solvent-induced PMF into different spatial regions suggests that TIP4P-FQ has stronger temperature dependence; the opposing destabilizing/stabilizing contributions from intertube water and more distal water balance each other and suppress the temperature dependence of total association free energy. Further investigation of hydrogen bonding network in intertube water reveals that TIP4P-FQ retains fewer hydrogen bonds than SPC/E, which correlates with the lower water number density in this region. This reduction of hydrogen bonds affects the intertube water dipoles. As the intertube volume decreases, TIP4P-FQ dipole moment approaches the gas phase value; the distribution of dipole magnitude also becomes narrower due to less average polarization/perturbation from other water molecules. Our results imply that the reduction of water under confinement may seem trivial, but underlying effects to structure and free energetics are non-negligible. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4892566>]

I. INTRODUCTION

The hydrophobic effect plays an important role in many natural phenomena including processes ranging from the observed separation of oil/water mixtures, protein folding, and the aggregation and self-assembly of hydrophobic entities such as micelles, bilayers, and monolayers.^{1–34} The rich, early history of molecular simulations exploring hydration of small hydrophobic molecules such as methane and noble gases^{17,35–43} is now continually updated with current state-of-the-art studies focused on larger and more chemically complex models of hydrophobes.^{38,41,42,44,45} These studies are further complemented by fundamental theory.²¹ The LCW theory and corroborating molecular dynamics simulations suggest a length-scale dependence for the nature of hydrophobic interactions. For small solutes, water is capable of undergoing slight distortions in the hydrogen bond network to accommodate the solvation of the solute. However, large solutes can significantly disrupt the hydrogen bond network. In particular rather intriguing notions of increased probabilities of empty volume (voids) coupled to long-range water-water correlations near hydrophobic surfaces have come to the forefront to consider the water-hydrophobe interface on a similar footing as the water liquid-vapor interface.^{46–49}

The use of simple, but importantly, computationally tractable, model systems such as hydrophobic plates

of varying sizes and roughness^{24,50–56} or nanotube-like materials,^{20,57} or model hydrophobic cavity-ligand systems^{58,59} have provided insights about solvent wetting/dewetting of hydrophobic surfaces, pulse-like solvent behavior through nanotubes, and the influence of solvent-hydrophobe interaction strengths on these behaviors. In many cases, the strength of water-water interactions has not been directly considered with regard to its effects on association of large hydrophobes. Indirectly, through the use of different water potentials, one can discern that there are no qualitative differences in the picture of hydrophobic interactions that arise from these studies.

Though numerous studies employing molecular simulations with today's state-of-the-art fixed-charge (additive) electrostatic models have appeared in the literature, there are relatively few studies of such effects on large hydrophobes using force fields that can modulate the molecular electrostatics in response to local environment—polarizable, or non-additive electrostatic force fields. The varying nature of electrostatics of water molecules in the condensed phase, at the liquid-vapor interface, and near hydrophobic and hydrophilic surfaces is dictated by quantum effects;^{60,61} moreover, there is a further subtlety associated with the dynamic nature of polarizability itself.⁶² Fixed-charge force fields are not able to capture this effect explicitly, stimulating questions about the implications of electrostatic polarization. Substantial recent work on the nature of water polarizability in condensed phases has demonstrated not only that the intrinsic polarizability of water molecules decreases in the condensed

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phase, but that there is a dependence on the local hydrogen bonding structure of the water molecule.^{62,63} With these ideas in mind, we consider in this paper the effects of varying solvent electrostatics on the hydrophobic interactions of large surfaces. Specifically, we consider single-walled carbon nanotubes (SWNT's) as our model hydrophobic systems. The possible applications of such carbonaceous materials to energy, environment,^{64–66} and human health^{64,67–70} are numerous and varied, and thus understanding fundamental aspects of these materials in aqueous systems (where they ultimately end up) is important and timely.^{66,71} We adopt additive models previously used to study such systems and non-additive (polarizable) models in order to present a systematic comparison. Regarding polarizable force fields currently pursued, force fields implementing Charge Equilibration (CHEQ),^{72–77} Drude-Oscillators,^{78–83} and Point-Dipole^{84–89} approaches to model polarizability are maturing, particularly enabled by advances in modern computational resources and decades of development efforts by various research groups. However, few studies on hydrophobic effects consider explicit treatment of polarizability.^{38,41,42} In this study, we compute the potential of mean force for association of two single-walled carbon nanotubes in two different atomistic models of water, one polarizable and the second non-polarizable. We consider the temperature dependence of this reversible work for association as well as an in-depth consideration of the various contributions to association free energetics arising from water in the various regions defined by the association geometry (to be discussed in detail below). Temperature dependence studies afford insight into the inherent contributions from enthalpy and entropy to the association process. We further address structural aspects of the solvent in the vicinity of the surfaces as well as the nature of the molecular electrostatics and its changes induced by the hydrophobes.

This study is organized as follows. In Sec. II we discuss the force fields and computational details. Our results are presented in Sec. III and are organized into four topics. We start with examining the density of water molecules in different spatial regions in Sec. III A. In Sec. III B we consider potential of mean force for nanotube association and the contribution from each component. The hydrogen bond and dipole moment profiles are investigated in Secs. III C and III D. We conclude our study in Sec. IV with a summary of our findings and general discussion.

II. METHODS

Molecular dynamics simulations were performed using the CHARMM package.⁹⁰ We adopt a simulation geometry that includes liquid vapor interface (LV) at the ends of a rectangular simulation box, with the two carbon nanotubes situated at locations within the water slab. This allows the system volume to adopt to the tubes. Simulations thus were performed in the NVT ensemble. The simulation cell was rectangular with dimensions of $L_x = 40$ Å, $L_y = 40$ Å, and $L_z = 150$ Å, in which z is the direction normal to the LV interface. Two (10,10) SWNTs are parallel and oriented along the x -dimension. The SWNTs are constructed with the Nanotube

TABLE I. Parameters used in the simulation.

	$R_{\min}$ (Å)	ϵ (kcal/mol)	q (e)
O(SPC/E)	3.5537	0.1554	−0.8476
O(TIP4P-FQ) ^a	3.5459	0.2862	
Tube ^b	4.0195	0.0663	0

^aThe charges for atoms on TIP4P-FQ fluctuate throughout the simulations.

^bThe LJ parameters for oxygen-tube interaction are fixed to be $\epsilon_{ij} = 0.1015$ kcal/mol, $R_{\min} = 3.7793$ Å for both water models.

Modeler package.⁹¹ Each (10,10) SWNT is comprised of 400 carbon atoms with the bond length of 1.421 Å.⁹² The diameter (D) and the length (l) of each tube are 13.56 Å and 24.0 Å, respectively. The Lennard-Jones (LJ) parameters of the tube atoms were $\epsilon = 0.0663$ kcal/mol, $R_{\min} = 4.0195$ Å, which are adopted from previous studies of hydrophobic systems;⁹³ however, the interactions among atoms on the same tube were excluded. Throughout the simulation the positions of all tube atoms were fixed. The water-tube interactions were fixed to be $\epsilon_{ij} = 0.1015$ kcal/mol, $R_{\min, ij} = 3.7793$ Å. These parameters are adopted from previous studies,⁹³ which have been validated to model hydrophobic effects in understanding the nature of surface friction in nanoscale fluid transport. A bulk slab consisting of 4800 water molecules, which are represented by the nonpolarizable extended simple point charge (SPC/E) model⁹⁴ or polarizable TIP4P-FQ model.⁷³ In order to obtain the potential of mean force (PMF) as a function of the separation between two SWNTs, we define the separation between two SWNTs (d) as the distance between the center of mass of the tubes (or the distance between the center axes of the tubes), as the order parameter of the PMF. In this study we sample more than 40 inter-tube separations ranging from 16.4 Å and 26.0 Å center of mass distance. For the SPC/E water the LJ parameters are $\epsilon_{OO} = 0.1554$ kcal/mol, $R_{\min} = 3.5537$ Å and are assigned only to the oxygen atom of water (see Table I). Point charges of oxygen and hydrogen atoms are $q_O = -0.8476e$ and $q_H = +0.4238e$, respectively. For simulations involving TIP4P-FQ water, $\epsilon_{OO} = 0.2862$ kcal/mol, $R_{\min} = 3.5459$ Å (also assigned only to the oxygen atom of water), and fictitious charge degrees of freedom with assigned masses of 0.000069 kcal mol^{−1} ps²/e². These charge degrees of freedom were coupled to a thermostat at 1 K with a mass of 0.005 kcal mol^{−1} ps² using the Nosé-Hoover method.⁹⁵

The polarizable water model, TIP4P-FQ,⁷³ is based on a charge equilibration formalism^{72,74,96} for which the electrostatic Hamiltonian is

$$E_{\text{elec}} = \sum_{i=1}^N (\chi_i + \Phi_i) q_i + \frac{1}{2} \sum_{i=1}^N \eta_i q_i^2 + \frac{1}{2} \sum_{i \neq j}^N J_{ij} q_i q_j, \quad (1)$$

where the parameters χ_i and η_i may be identified with atomic electronegativities and hardnesses, respectively; the J_{ij} terms represent a parameterized molecular Coulomb integral between pairs of atoms. Φ_i represents an external potential evaluated at each site i ; in this work, no explicit external electrical potentials are applied. Within this formalism, components of the molecular polarizability tensor are related to the inverse of the hardness matrix (constructed from the values of η_i and J_{ij} above) as $\alpha_{\beta\gamma} = \mathbf{R}_\beta \mathbf{J}^{-1} \mathbf{R}_\gamma$ where $\mathbf{R}_\beta$ represents the β

Cartesian components of the atomic position vector.⁹⁷ In this sense, the charge equilibration formalism is a true dipole polarizable potential model.

Constant temperature for the nuclear degrees of freedom (water molecules that are allowed to move freely) was maintained throughout the same simulation using the Nosé-Hoover thermostat with a mass of 50 kcal mol⁻¹ ps² for the thermostat degree of freedom. In this paper we studied the temperature dependence of tube association at 280 K, 300 K, 320 K, 340 K, and 360 K.

Since a small number of total system atoms are held fixed, thus possibly influencing the dynamics of water molecules in the immediate vicinity of the tube atoms, we considered two factors to assess the validity of the use of the Nosé-Hoover thermostat in this particular system. In the supplementary material (Figures S1–S3),⁹⁸ we compute the velocity distributions of the *x*, *y*, and *z*-components of the oxygen atoms of water molecules in bulk region and in the first solvation layer of the hydrophobes. We also calculate the temperature of the water molecules in bulk and in the first solvation layer of the tube atoms to make certain that the system in equilibrium does not violate equipartition of kinetic energy. The test is based on parallel plate geometry using the same water-hydrophobe interaction parameters as used in this study. The geometry of the plates can be found in Zangi *et al.*⁹⁹ or Bauer *et al.*¹⁰⁰ In order to compare the temperature distribution of water near the hydrophobe and in the bulk using similar sampling volume, the geometry of a plate is more convenient than the geometry of a nanotube. This geometrical difference should not induce any difference in the temperature distribution of vicinal water molecules.

The non-bond interactions were treated via the standard Lennard-Jones “12-6” potential

$$E_{\text{LJ}} = \sum_{ij} \varepsilon_{ij} \left(\frac{R_{\text{min},ij}^{12}}{r_{ij}^{12}} - 2 \frac{R_{\text{min},ij}^6}{r_{ij}^6} \right). \quad (2)$$

Lennard-Jones interactions were gradually switched off at interparticle distance of 12 Å, with a gradual switching between 11 Å and 12 Å using the switching function

$$S(r_{ij}) = \begin{cases} 1 & r_{ij} \leq r_{\text{on}} \\ \frac{(r_{\text{off}}^2 - r_{ij}^2)^2 (r_{\text{off}}^2 + 2r_{ij}^2 - 3r_{\text{on}}^2)}{(r_{\text{off}}^2 - r_{\text{on}}^2)^3} & r_{\text{on}} < r_{ij} \leq r_{\text{off}} \\ 0 & r_{ij} > r_{\text{off}} \end{cases}. \quad (3)$$

Conditionally convergent long-range electrostatic interactions were treated using Particle Mesh Ewald (PME)¹⁰¹ approach with a 40 × 40 × 150 point grid and $\kappa = 0.330$. SHAKE¹⁰² was used to maintain the rigid geometry of each water molecule. Dynamics were propagated using a Velocity-Verlet integrator with a 1.0 fs timestep for nonpolarizable SPC/E and 0.5 fs for TIP4P-FQ under 3D periodic boundary conditions. All MD trajectories were stored with a saving frequency of 500 fs for the consecutive analyses. The sampling time for each window for both models used was at least 11 ns. Properties were calculated from all but the first 1 ns, which was treated as equilibration, resulting in more than 10 ns at each temperature per window for data analyses.

III. RESULTS

A. Spatial distribution of solvent

We address water distribution around the nanotubes in this section. We define three spatial regions based on the geometry of our systems, shown in Figures 1(b)–1(d). For the water molecules within the inter-tube region (R_1 , as shown in Figure 1(b)), we define a rectangular sampling volume. The length (L) of the volume is along the *x*-axis with $-l' \leq x \leq l'$ ($l' = 11.0$ Å), which makes $L = 22.0$ Å, which is shorter than the tube length. The selection along the tube dimension is slightly reduced from the true length of the tube to reduce artifacts arising from the edge of the tubes. The width (W) is along the *z*-axis and determined by subtracting the tube diameter from the tube separation (d). The height (H) equals $D - 2R_{\text{min,OC}}$ and projects along the *y*-axis. The next region (R_2) considers water molecules within the cylindrical tubes illustrated in Figure 1(c). The center axis is along the *x*-axis, and the sampling volume is $-l' \leq x \leq l'$. Finally, R_3 includes regions other than R_1 and R_2 , as shown in Figure 1(d). In order to distinguish the physical properties of water near the nanotubes and water in the bulk, we usually use a half cylindrical sampling volume on the side of the tube extending into the bulk (which will be discussed in Secs. III B–III D) instead of R_3 .

We begin with R_1 by plotting the profile of the average number of water oxygens in the intertube rectangular region ($\langle N_{\text{water}, R_1} \rangle$) as a function of tube separation d in Figure 2(a) (for SPC/E) and Fig. 2(b) (for TIP4P-FQ). In general, the intertube volume increases and includes more water molecules

FIG. 1. Representative snapshots of the system used in this study; separation between the center axes of the tubes is 26.0 Å. The diameter and the length of each tube are 13.56 Å and 24.0 Å, respectively. Atom types can be distinguished by the following color code: O (red), H (white), tube atoms (blue). (a) Side profile showing the relative solvation of the tubes in the normal and lateral directions. Projection of tubes with predefined water region (b) R_1 (c) R_2 (d) R_3 on *y* – *z* plane. Refer to main text for the definition of *W*, *H*, and *L*.

FIG. 2. Average number of confined water in the intertube region using (a) SPC/E (b) TIP4P-FQ water model. Panel (c) shows the excess, defined as $\langle N_{\text{SPC/E}, R_1} \rangle - \langle N_{\text{TIP4P-FQ}, R_1} \rangle$. The inset highlights the detail in critical separation. Average number of water in the intratube region using (d) SPC/E (e) TIP4P-FQ water model. Uncertainties were obtained as the standard deviation over time average. Panel (f) shows the excess in the intra-tube region; the uncertainties were estimated using the geometric combination rule. Radial density profile of water using (g) SPC/E (h) TIP4P-FQ. Panel (i) shows the excess. Red arrows indicate from low temperature to high temperature.

as the tube separation increases; there are drastic increments when $19 \text{ \AA} \leq d \leq 20 \text{ \AA}$ and $22 \text{ \AA} \leq d \leq 23 \text{ \AA}$, indicating possible free energetic barriers at these critical tube separations. Plateaus of $\langle N_{\text{water}, R_1} \rangle$ suggest the existence of stable solvation shells at particular tube separations, which are also found in other instances of hydrophobic association.^{44,103} We plot the water oxygen density profile along z -dimension at 300 K and 360 K in Figure 3 to further illustrate this behavior. Each

FIG. 3. Density profiles of intertube water oxygen along z -axis, for (a) SPC/E (b) TIP4P-FQ cases. Straight lines indicate the profiles at 300 K, while dashed line refer to the profiles at 360 K. A vertical offset of $0.12 \text{ \AA}^{-3}$ is added for clarity.

$z \sim z + dz$ region has the same x - and y -dimension length resulting in a sampling volume of $L \times H \times dz$. Straight lines indicate the density profiles at 300 K, while dashed lines refer to the profiles at 360 K. For both water models, the second solvation shell of water (the peak at $z = 0 \text{ \AA}$ for tube separation $d = 26.0 \text{ \AA}$ in Figure 3) only appears at the largest separation, therefore the total number of $\langle N_{\text{water}, R_1} \rangle$ is determined by the first solvation shell. At the same tube separation, the density of water at low temperature is substantially larger than the density at high temperature. Giovambattista *et al.* also found the same behavior for the water confined between two hydrophobic plates.¹⁰⁴

We define excess intertube water as $\langle N_{\text{SPC/E}, R_1}(d) \rangle - \langle N_{\text{TIP4P-FQ}, R_1}(d) \rangle$; this is displayed in Figure 2(c). This value is positive for all values of the order parameter indicating more SPC/E observed in R_1 . The largest difference occurs at $d \sim 19.5 \text{ \AA}$ (as emphasized in the inset), where four to six more SPC/E than TIP4P-FQ waters are observed; the maximum in the excess curve reduces as temperature increases (increasing temperature is indicated by the direction of the arrow in Figure 2(c)), and slightly shifts to larger tube separations. The peak in excess water molecules suggests a larger critical tube-tube separation to fill the interior region for the polarizable TIP4P-FQ model than nonpolarizable SPC/E, which recapitulates the comparison among various water models confined between two hydrophobic plates reported by Bauer and Patel.¹⁰⁵

In previous studies, the process of associating two hydrophobic surfaces usually displays a dewetting transition where the water confined between the two surfaces is

unstable in its liquid state and evaporates.^{54,99,105,106} This transition has been shown to correlate with the equivalent well depth of water-carbon interaction.^{107,108} As the geometry of nanotubes deviates from the planar geometry of plates used in previous studies, thus making the definition of a suitable region within which to consider any dewetting phenomena, further discussion regarding this dewetting transition is not pursued in this paper. We include some of the time profiles for numbers of intertube water in the supplementary material (Figure S4).⁹⁸

In Figures 2(d) and 2(e) we present the water profiles in region R_2 versus temperature changes. Each value indicates the average number of water molecules in each CNT ($\langle N_{\text{water}, R_2} \rangle$) at the corresponding temperature, along with the uncertainty obtained via the standard deviation over the time average. These values are independent from the tube separation. The excess between two water models ($\langle N_{\text{SPC/E}, R_2} \rangle - \langle N_{\text{TIP4P-FQ}, R_2} \rangle$) reveals a five-water difference for region R_2 which weakly depends on the temperature if we consider the uncertainties.

Finally we compare the radial number density profiles of water molecules about the tube to depict the distribution of solvent in the outer tube region. We restricted sampling for these profiles to a half cylinder on the side of the tube extending into the bulk, in order to prevent the sampling between the nanotubes, where the solvent distributions will contain interference effects from the other tube. We reiterate that this does not equal to the region R_3 . After each half cylinder is considered (for each tube) the symmetry of the two-tube system allows us to combine the sampling volumes into a full cylinder. We limited the length of the sampling cylinder to $-l' \leq x \leq l'$ ($l' = 11.0$ Å), in order to avoid artifacts arising from the edge of the tubes. So the radial density profiles ($\rho(r)$) can be written as

$$\rho_i(r) = \frac{N_i}{4\pi l' r dr}, \quad (4)$$

where i is the atomic/molecular species (here we choose water oxygen atoms), N_i is the corresponding number of species i within the region $r - dr/2$ to $r + dr/2$. The results for SPC/E and TIP4P-FQ are displayed in Figures 2(g) and 2(h). Since our focus is the outer shell of the tube, we only plot the results for $r \geq 8$ Å. Enhanced water density was found in the first solvation shell of the nanotubes, in agreement with a preponderance of published data concerning first solvation shell ordering around large hydrophobes.^{109–111} Interestingly, when we consider the excess ($\rho_{\text{O, SPC/E}}(r) - \rho_{\text{O, TIP4P-FQ}}(r)$), the value changes its sign from negative to positive as the temperature increases, as displayed in Figure 2(i). In other words, TIP4P-FQ model is presenting a relatively stronger temperature dependence than SPC/E. We list our calculated, water number density in bulk environment at different temperatures in Table II, acknowledging that our values are somehow slightly larger than in previous studies^{112–114} which might be related to the selection of NVT ensemble and the presence of hydrophobes. The different temperature dependencies for outer densities are also evident in the differences in the change of the first-peak heights in the density profiles of panels (g) and (h) of Figure 2.

TABLE II. Selected bulk properties for SPC/E and TIP4P-FQ at different temperatures. Values in parentheses denote the uncertainty in the last reported digit as determined from the standard deviation.

System	ρ_o (Å ⁻³)	$\langle N_{\text{HB}} \rangle$	μ (D)
SPC/E			
280 K	0.0339(11)	3.63(5)	2.39
300 K	0.0335(8)	3.54(5)	2.39
320 K	0.0330(6)	3.45(5)	2.39
340 K	0.0325(4)	3.36(5)	2.39
360 K	0.0320(4)	3.27(5)	2.39
TIP4P-FQ			
280 K	0.0344(20)	3.68(6)	2.68
300 K	0.0338(15)	3.56(5)	2.62
320 K	0.0319(10)	3.43(5)	2.57
340 K	0.0303(8)	3.29(5)	2.52
360 K	0.0276(6)	3.16(5)	2.48

B. Potential of mean force

We next address the free energetics of nanotube assembly. The PMF for nanotube association following an order parameter that brings the parallel-oriented tubes from an infinite-separation, dissociated state to the associated, contact state is calculated directly from the average forces acting on a tube,

$$W(\xi) = - \int \langle F(\xi) \rangle d\xi, \quad (5)$$

where ξ is the order parameter taken as the separation distance between the center-of-mass of the two CNTs (d). We consider the average of forces ($\langle F(\xi) \rangle$) acting on each nanotube over the sampled configurations at each separation distance; the average force used in the integration is the average of the values for the two CNTs after negating the forces acting on the CNT located in the negative z -region of the simulation cell. All profiles of the PMF are shifted such that $W(\xi_{\text{dissociated}}) = 0$ kcal/mol. We denote the difference in PMF from dissociated state to the global minimum,

$$\Delta W = W(\xi_{\text{contact}}) - W(\xi_{\text{dissociated}}), \quad (6)$$

where $\xi_{\text{contact}} \sim 16.9$ Å (position of tube contact minimum) and $\xi_{\text{dissociated}} = 26.0$ Å (dissociated distance). We show the PMFs for SPC/E and TIP4P-FQ in Figures 4(a) and 2(b), respectively. The insets emphasize PMF profiles near the contact state. We reiterate that the interactions involving the CNTs are fixed to be equivalent across all systems studied so differences in the PMF for different water models are determined by the solvent.

In general, less favorable interaction between CNTs is observed in the nonpolarizable model. This is consistent with previous studies comparing the association between methanes³⁸ or hydrophobic plates¹⁰⁵ with different water models. Usually it is related to the number of waters between the hydrophobes; we will address this later. As temperature increases, the PMF shows more stability. We calculated ΔW as function of temperature (Figure 4(c)); the linear fitting

FIG. 4. Potential of mean force for nanotube association in (a) SPC/E (b) TIP4P-FQ at different temperature. Insets show the focused profiles near the contact state. Panel (c) shows $\Delta W(\text{contact state})$ as a function of temperature. Red arrows in the insets indicate from low temperature to high temperature.

results between ΔW versus temperature are

$$\begin{aligned}\Delta W_{\text{SPC/E}} &= -0.0762T - 21.58, \\ \Delta W_{\text{TIP4P-FQ}} &= -0.01625T - 54.67.\end{aligned}\quad (7)$$

Interestingly, in another study using two hydrophobic plates (diameter ~ 21 Å) with the SPC/E model performed by Zangi and Berne,²⁴ the slope of stability versus temperature (-0.032 kcal mol⁻¹ K⁻¹) is smaller than our result, though the behaviors of plates and nanotubes are qualitatively similar. In an earlier work by Mancera and Buckingham, the authors reported the aggregation of ethane in aqueous solution has a different dependence with temperature, in which they found at the intermediate temperature of 317 K ethane particles have the maximum tendency to aggregate.¹¹⁵ This reflects the difference in solute size between ethane and the model hydrophobes in Zangi's and our work, since the thermodynamic driving force (enthalpic or entropic) is length-scale dependent.^{16,116} We admit that the comparison of absolute slopes between our system and the work of Zangi *et al.*⁹⁹ might not be meaningful. However, our results are qualitatively consistent with their work.

The free energy of association is found to be less temperature dependent using the polarizable TIP4P-FQ model, as shown with smaller slope in Eq. (7). This is somehow counter-intuitive considering the stronger temperature dependencies in spatial distribution of TIP4P-FQ. Since the CNT atoms are neutral, the only way water molecules can apply forces to the CNT atoms is via van der Waals interactions. Thus, from the mechanistic point of view, if the net force on a CNT from a single water is positive (destabilizing), the water molecule can be treated as “destabilizing water”; on the other hand, water is “stabilizing water” if the sum of forces is negative (stabilizing). This classification of water molecules is related to the position of the species;¹¹⁷ for example, the waters confined between two hydrophobes are shown to work against the dimerization of hydrophobes.^{44,105} We include a force map in the supplementary material (Figure S5)⁹⁸ to illustrate how the position of a water molecule defines its contribution to CNT association in terms of its stabilizing/destabilizing influence; the force map is independent of temperature and water model (since the tube-water interaction is fixed).

Since the tube coordinates are fixed throughout the course of the simulation for each separation distance and the

tube-tube interactions are the same in all systems, the tube contribution is the sole contributor to non-solvent induced PMF; i.e., the solvent-induced contribution to the PMF can be written as $\Delta W_{\text{solv}} = \Delta W - \Delta W_{\text{non-solv}}$. Hence we divide ΔW_{solv} into

$$\Delta W_{\text{solv}} = \Delta W_{\text{solv},R1} + \Delta W_{\text{solv},R2} + \Delta W_{\text{solv},R3}. \quad (8)$$

The results are shown in Figure 5. We next discuss the contribution from each region.

From Figures 5(a) and 5(d), $\Delta W_{\text{solv},R1}$ is destabilizing for both water models for all values of the order parameter. Although at separations below 19 Å both SPC/E and TIP4P-FQ in R_1 show unfavorable contributions, there are actually no water molecules between the tubes. This leads to a flat profile for $\Delta W_{\text{solv},R1}$ when d is less than 19 Å. Between $d = 19$ –20 Å (as depicted with grey dotted lines), $\Delta W_{\text{solv},R1}$ falls drastically, corresponding to an increase of $\langle N_{\text{water},R1} \rangle$. This reduction in $\Delta W_{\text{solv},R1}$ is not as sharp in TIP4P-FQ, and this correlates with the smoother transition in water number between the tubes as shown in Figure 2(a) versus Figure 2(b) (for SPC/E versus TIP4P-FQ). The smoother transition results from TIP4P-FQ water model's ability to adapt to its environment by modulating its electrostatic properties. This ability prevents an abrupt transition in water number compared to the behavior of SPC/E. This behavior has been described in earlier work as well.¹⁰⁵ Finally, note that the temperature dependence of $\Delta W_{\text{TIP4P-FQ},R1}$ near the barrier ($d \sim 21.5$ Å) is stronger than $\Delta W_{\text{SPC/E},R1}$, which is different from the behavior of the total PMF.

Figures 5(b) and 5(e) show solvent contribution to PMF from region R_2 . Both water models present stabilizing contributions. SPC/E is slightly more stabilizing than TIP4P-FQ at small separations. This is a consequence of there being more stabilizing SPC/E waters present at small tube separations. When the CNTs are close, water molecules in one tube can apply force to the other tube since the atomic distances are within the cutoff scheme. This contribution is stabilizing considering the attractive van der Waals interaction; when tubes are sufficiently separated, all the water molecules in the tube are beyond the cutoff (of force calculation) from the other tube. Although $\Delta W_{\text{TIP4P-FQ},R2}$ appears to show stronger temperature dependence than $\Delta W_{\text{SPC/E},R2}$, the difference is small (~ 1 kcal/mol) in scale.

FIG. 5. Decomposition of water induced potential of mean force into different regions. The gray dotted lines indicate the critical tube separations ($d = 19\text{--}20\text{ \AA}$) for water molecules to access the inter-tube region R_1 .

Figures 5(c) and 5(f) illustrate the contribution of water in region R_3 . Insets emphasize tube separations between $17\text{ \AA}$ and $20\text{ \AA}$. $\Delta W_{\text{TIP4P-FQ},R_3}$ shows more temperature dependence. For the range of order parameter studied, the contribution is negative (stabilizing). There is a big difference in magnitude between two models. When $d \geq 20\text{ \AA}$, $\Delta W_{\text{SPC/E},R_3}$ becomes more stabilizing as the tube separation decreases. $\Delta W_{\text{SPC/E},R_3}$ flattens at the critical separations ($19\text{ \AA}$ – $20\text{ \AA}$), then falls slightly again when $d \leq 19\text{ \AA}$. On the other hand, $\Delta W_{\text{TIP4P-FQ},R_3}$ falls smoothly as the tube separation decreases.

To summarize, we decomposed the water contribution to nanotube association into three regions based on the geometry of our system. Although the total solvent contribution from polarizable TIP4P-FQ exhibits weak temperature dependence, its decomposition reveals that contributions from R_1 and R_3 both display stronger dependencies on temperature. As temperature increases, the number of water molecules that can affect the tube association (i.e., within the calculation cutoff such that the water can apply forces to tube atoms) falls for both R_1 and R_3 ; consequently, the contributions to tube association for these two regions become lower in magnitude. Waters in the intertube R_1 region destabilize the nanotube association, while waters in R_3 tend to contribute in a stabilizing manner; therefore, as the system temperature increases, $\Delta W_{\text{water},R_1}$ becomes less destabilizing, while $\Delta W_{\text{water},R_3}$ becomes less stabilizing. In both intertube and outer regions, solvent contributions from polarizable TIP4P-FQ reveal stronger dependencies with temperature, but the contributions from these two regions offset one another, leading to barely any temperature dependence for total PMF.

From the previous discussion, it is shown that the polarizable TIP4P-FQ is structurally more temperature dependent

than nonpolarizable SPC/E, even when we consider the presence of hydrophobes in the system. Our next goal is to illustrate the temperature response between intertube water and bulk water, in order to further differentiate the effects from solvent polarizability.

C. Hydrogen bond profiles

Hydrogen bonding is especially relevant to understanding water properties for its sensitivity to the surface environment. In general, there are two methods to define hydrogen bonds in simulations: by interaction energy¹¹⁸ or relative geometry between a pair of water molecules. The choice of geometric criteria is generally preferred for providing more reliable results than energetic criteria in simulation studies.^{119,120} In this paper, two water molecules are considered hydrogen bonded if the oxygen-oxygen distance is less than $3.5\text{ \AA}$ and the $\text{HO}\cdots\text{O}$ angle is less than 30° .^{105,117,119}

We use the sampling volume for radial density profiles to calculate the average numbers of hydrogen bonds per water ($\langle N_{\text{HB}} \rangle$), as functions of the (radial) distance from tube axes. The results using SPC/E and TIP4P-FQ are shown in Figures 6(a) and 6(b), respectively; the average values of $\langle N_{\text{HB}} \rangle$ in bulk environment are listed in Table II. As the temperature increases, less hydrogen bonds per water are formed in bulk solvent. It can be seen both in Figure 6 and Table II that polarizable TIP4P-FQ again shows stronger temperature dependence than nonpolarizable SPC/E. This is because the interaction between TIP4P-FQ water molecules depends on local environment, such as local density. In situations where the density changes, the polarizability of the model allows for the electrostatic component of the water-water interaction to change, thus leading to perhaps subtle, but non-trivial

FIG. 6. Average number of hydrogen bonds as functions of r at different temperatures for (a) SPC/E (b) TIP4P-FQ. The hydrogen bonding profile for water in the intertube region using (c) SPC/E (d) TIP4P-FQ. Red arrows indicate from low temperature to high temperature. A vertical offset of 4 is added for clarity.

manifestations in structure and free energetics. The influence of this non-additivity is evident on hydrogen bonding patterns. In the vicinity of the nanotubes, the environment is liquid-vapor like; water exhibits orientational preference (as evidenced in Figure S6 of the supplementary material⁹⁸), which therefore limits the possibilities for hydrogen bond connectivity and results in a depletion layer of hydrogen bonds near the tube surface.^{24,121}

We next examine hydrogen bond profiles of water within the intertube region. The z -dependent profiles at several tube separations, using the sampling volume defined in Figure 3, are displayed in Figures 6(c) and 6(d). The bulk values of $\langle N_{\text{HB}} \rangle$ at the corresponding temperature are also included to illustrate and compare the intertube environment using two water models. At the dissociated separation, both water models present a wide region of hydrogen bonding profile which is similar with bulk solvent. At $d = 23$ Å, SPC/E still displays such region at both 300 K and 360 K; however, the hydrogen bond per water using TIP4P-FQ at 360 K does not reach its bulk value. This deviation in hydrogen bonding network between intertube region and bulk solvent becomes severe as the tube separation decreases. We also observe that, at the same

separation, SPC/E always demonstrates more hydrogen bonds than TIP4P-FQ.

Based on the definition of hydrogen bonds, the reduction of hydrogen bonds can be either due to geometrical changes of coordinated water (i.e., as they relate to the chosen distance criteria) or the angle between water molecules fails to fulfill the angular criteria. In other words, there are two possible scenarios for the reduction of hydrogen bonds: the first is simply the loss of coordinated water within 3.5 Å for each water; the second scenario is that there are same amount of coordinated water molecules but angles between water molecules are much larger than 30 degree. In the supplementary material (Figure S7)⁹⁸ we include the distribution of angles between water molecules, when the water is in the bulk environment or intertube region (R_1). For the same temperature this angular distribution is independent of tube separation for both SPC/E and TIP4P-FQ, indicating that the distance criteria (≤ 3.5 Å) is the determining factor in causing the loss of hydrogen bonds. We therefore focus on the discussion about how the quantity of coordination water influences hydrogen bonds. Figure 7 shows the distribution of coordination number (N_{coord}) for waters in different condition. When water is in

FIG. 7. Distribution of coordinated water using SPC/E water model (a) in the bulk and intertube regions at (b) 300 K (c) 360 K. Distribution of coordinated water using TIP4P-FQ water model (d) in the bulk and intertube regions at (e) 300 K (f) 360 K.

the bulk (panels (a) and (d)), both water models exhibit similar distribution. As temperature increases, the distribution becomes slightly wider.

When a water is in R_1 region, the distribution shifts to lower N_{coor} as the tube separation decreases. In Figures 7(b), 7(c), 7(e), and 7(f), we plot the distribution of N_{coor} for bulk environment at the corresponding model and temperature as the reference to compare the modified distribution at each tube separation. In the case of TIP4P-FQ, the distribution of N_{coor} always shifts more from bulk distribution than SPC/E does when we consider the same tube separation.

D. Dipole moment profiles

Polarizable models possess the ability to dynamically induce a dipole moment. Examining the dipole moment profiles in the intertube region is helpful to understand the different intrinsic hydrophobicity caused by varying tube separations and water models.

The dipole moment of a water is computed by

$$\vec{\mu} = \sum_i \vec{r}_i q_i. \quad (9)$$

Here $\langle \mu(r) \rangle$ is then the average of the magnitude of $\vec{\mu}$. We use the sampling volume for radial density profiles to calculate the $\langle \mu(r) \rangle$ as functions of the radial distance from tube axes. The results are shown in Figure 8(a). The water dipole moment reduces as the water approaches the nanotube surface, which was also observed in our previous study.¹⁰⁵ $\langle \mu_{\text{bulk}} \rangle$ at different temperatures are listed in Table II. The water dipole moment along z -dimension for the intertube region is presented in Figures 8(b) and 8(c) for 300 K and 360 K. Only at $d = 26$ Å is intertube water able to reach the same dipole moment mag-

nitude as bulk water. As the tube separation decreases, the dipole moment decreases to the value of the gas phase dipole moment in vacuum (TIP4P-FQ is parametrized to reproduce the experimental value of 1.85 D^{73}).

The distributions of μ for water in different environments are presented in Figures 9(a)–9(c). We start with the distribution of bulk dipole moment, as shown in Figure 9(a). As temperature elevates, the distribution shifts to lower μ and becomes slightly sharper. The weakened hydrogen bonding network (as shown in Figure 7(b) or Table II) lessens the polarization of water molecules, therefore decreases the dipole moments. Regarding the width of the distribution, previous studies using *ab initio* molecular dynamics predicted a wider distribution of dipole moment magnitude at higher temperature;^{122,123} Kang *et al.* consider the distribution of dipole moments related to the extent of intramolecular charge fluctuations.¹²³ However, these studies focused on the spectrum from room temperature to supercritical conditions, thus beyond the scope of current work. We suggest the sharpened distribution of dipole moment is due to lower solvent density at higher temperature. At 360 K, the highest temperature of this work, the hydrogen bonding network is still structurally similar with that at lower temperature according to our previous discussion. Hence, less perturbation to the polarization of water molecules is expected, which results in narrower distribution of water dipole moments.

In Figures 9(b) and 9(c) we present the distribution of dipole moments for water in the intertube region at 300 K and 360 K. At 300 K, with decreasing tube separation, the distribution shifts to lower dipole moments and sharpens. This result is expected as in the vicinity of the hydrophobe, dipole moments drop; at smaller tube separations, sampling volume is compressed, thus the width of distribution of water

FIG. 8. (a) Average dipole moment magnitude as a function of r at different temperatures for TIP4P-FQ. Dipole moment profiles for TIP4P-FQ water models over a range of plate separation distances along the z -axis at (b) 300 K (c) 360 K. Dashed lines represent the average value of bulk dipole moment. A vertical offset of 0.1 D is added for clarity.

dipole moments becomes narrower as the effects from the hydrophobe increase. At 360 K, the distribution width generally compresses as the tube separation reduces, in a less significant manner. The separation of $d = 19.4$ Å is the only exception; the width of dipole moment distribution does not become sharpened. We consider this exception correlated with the reduction of water molecules in the confined region at this temperature. In the supplementary material (Figure S8)⁹⁸ we include the distribution $P(N_{\text{TIP4P-FQ}, R_1})$ of having $N_{\text{TIP4P-FQ}, R_1}$ water molecules in region R_1 ; the peak happens at having only 1 TIP4P-FQ at high temperature, while at low temperature the configurations of having 2 TIP4P-FQ in R_1 are more robust. Thus, conceptually there is a higher possibility to mimic the gas phase environment for intertube region at high temperature, which is evidenced by the (ten-times) larger probability for TIP4P-FQ in R_1 to exhibit the dipole moment of 1.85 D at 360 K than at 300 K.

We next address the intertube water orientation by defining ϕ as the angle between $\vec{\mu}$ and z -axis. Due to the geometry of our two-tube system, we symmetrized the dipole direction such that the value of $\cos \phi$ is between 0 and 1. In this convention, water dipole is parallel to the z -axis when $\cos \phi$

$= 1$; water dipole is perpendicular to z -axis when $\cos \phi = 0$. Figure 9(d) shows the distribution of $\cos \phi$ for water in the bulk; as expected, all orientations are equally probable. We use R_1 as the same sampling volume for this calculation for intertube water. When water molecules are under confinement, the distribution changes, as shown in Figures 9(e) and 9(f) for several tube separations at 300 K and 360 K. In general, probabilities of large $\cos \phi$ values reduce; configurations with small $\cos \phi$ are more probable. Similar orientational profiles for SPC/E dipole are included in the supplementary material (Figure S9).⁹⁸ However, when $d = 23.0$ Å at 300 K, the distribution is behaving differently with a more probable orientation at $\cos \phi = 0.5$ (as emphasized with purple arrow in Figure 9(e)). This is related to the intertube solvation structure shown in Figure 3. When $d = 21.0$ Å, the intertube density shows a plateau, indicating no predominant influence from either tube in this region; i.e., the effect from one tube to the water dipole orientation is balanced by the effect from the other tube. Thus, the water dipoles are preferred to be perpendicular to z -dimension. This is further supported from the comparison between the intertube $P(\cos \phi)$ for SPC/E and TIP4P-FQ (Figure S9 of the supplementary material⁹⁸); SPC/E shows

FIG. 9. Distributions of dipole moment magnitude (a) in the bulk and intertube regions at (b) 300 K (c) 360 K. Distributions of dipole moment direction (relative to z -axis) (d) in the bulk and intertube regions at (e) 300 K (f) 360 K.

increasing efficacy of $\cos \phi = 0$ since its intertube density is larger than TIP4P-FQ at $d = 21.0$ Å. At tube separation $d = 23.0$ Å, two severely ordered, separated solvation shells are formed in the intertube region; the density of water at the very center of R_1 is small. In the meantime, because of the curvature of nanotube surface, the configurations perfectly parallel to z -dimension are less likely. Consequently, $P(\cos \phi)$ reduces on both ends ($\cos \phi = 0$ or 1), and eventually promotes the intermediate angles. As temperature increases, the solvation shells for the intertube region are less-ordered (shown in Figure 3), and therefore the maximum of $P(\cos \phi)$ disappears.

IV. SUMMARY AND CONCLUSIONS

In this work, we have presented molecular dynamics simulation results of association between two single-walled carbon nanotubes with nonpolarizable SPC/E and polarizable TIP4P-FQ water models, in the temperature range between 280 K to 360 K. Based on our system geometry, the behaviors of water is investigated with three partitions: intertube, intratube, and outer regions. Analyses of number densities and hydrogen bonding profiles in these regions demonstrate stronger temperature dependencies using polarizable TIP4P-FQ water model; however, the PMF calculations of nanotube association with TIP4P-FQ is more favorable and reveal a relatively weaker connection with temperature. Decomposition of PMF from the three predefined regions signified that in both intertube and outer regions, solvent contributions from polarizable TIP4P-FQ reveal stronger dependencies with temperature. Intertube water destabilizes the nanotube association, while water in outer regions contributes oppositely; thus contributions of TIP4P-FQ from these two regions basically balance each other and suppress the temperature dependence of total association free energy.

Solvent structures and dipole moment profiles in the intertube region are also examined to further differentiate the effects of including water polarizability in our simulations. The variation of tube separation indicates different environment/confinement between the nanotubes. Intertube TIP4P-FQ explicitly has fewer hydrogen bonds than intertube SPC/E under the same tube separation, by virtue of the lower number of water (density) in this region along with the ability of TIP4P-FQ water to modulate its molecular electrostatics. This change in hydrogen bonding network also affects the intertube water dipoles. As the intertube volume decreases, the TIP4P-FQ dipole moment magnitude approaches the gas phase dipole moment in vacuum; the distribution of dipole magnitude also becomes narrower due to lesser polarization/perturbation from other water molecules arising from the lower intertube water density.

Our results imply that incorporating polarizability in simulations does provide different physical insights. The reduction of water density under confinement may seem trivial, but the underlying effects to structures and free energetics are non-negligible. This warrants further continuing investigation on how solvent (and later solute) polarization effects in biological contexts, e.g., protein assemblies, as the inherent chemical and topographical heterogeneities of biomacromolecules are more complicated than our simple two-hydrophobe system.

ACKNOWLEDGMENTS

The authors acknowledge support from the National Science Foundation (CAREER:MCB:1149802). Computational resources are acknowledged via support from National Institutes of Health (NIH) (COBRE:P20-RR015588) in the Chemical Engineering Department at the University of

Delaware and (COBRE:5P20RR017716-07) at the University of Delaware, Department of Chemistry and Biochemistry. S.P. thanks N. Patel for fruitful discussion and encouragement for the duration of this work.

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