Communication

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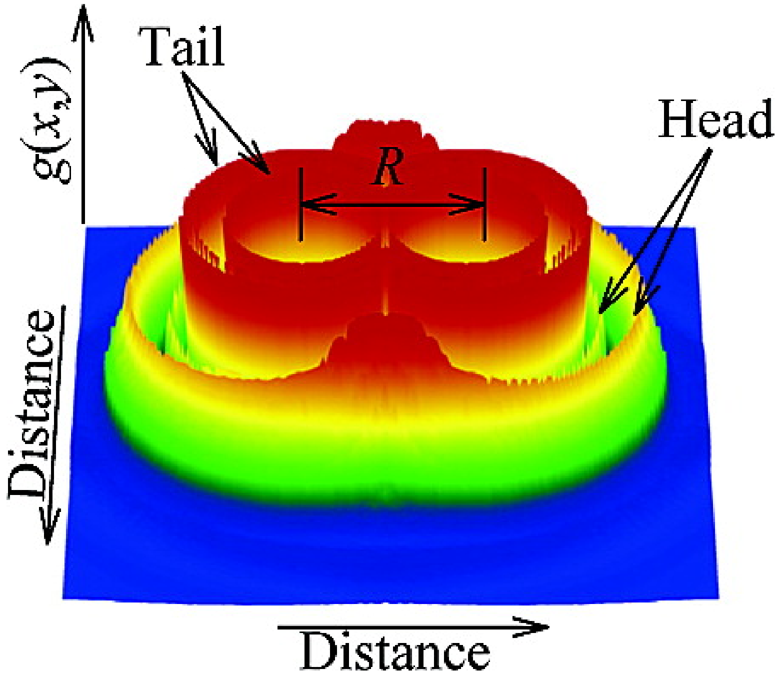

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# Dispersing Nanotubes with Surfactants: A Microscopic Statistical Mechanical Analysis

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We present the first statistical mechanical study of carbon nanotube (CNT) interactions in aqueous solutions of ionic surfactants. This work is motivated by the following recent experimental observations. First, stable CNT dispersions can be prepared at surfactant concentrations below the critical micelle concentration (CMC).[1] Second, small-angle neutron scattering (SANS) indicates that surfactants absorb onto the CNT surface in a random fashion.[2] This observation contradicts a previous conjecture that surfactants form cylindrical micelles centered on CNT cores.[3] In view of this controversy, and given that surfactants provide one of the most efficient and nonintrusive ways of preparing stable CNT dispersions, it is of utmost importance to develop a microscopic understanding of the mechanism of stabilization.

Although simulations of cylindrical sodium dodecyl sulfate micelles with CNT cores have been previously performed,[4] the only existing theoretical study of CNT stabilization in solutions is due to Szleifer and co-workers, who used mean-field theory to compute the potential of mean force (PMF) between two CNTs stabilized by grafted polymer chains.[5] The computed PMF displayed a substantial repulsive barrier (located outside of the deep van der Waals minimum[6]), whose height increased with coverage and chain length as is common for steric stabilization. In the case of ionic surfactants, the barrier in the PMF primarily arises because of the repulsion between like-charged heads. The major goal of this work is to compute this PMF from a microscopic statistical mechanical theory.

We adopt the familiar McMillan−Meyer-type approach,[7] where the solvent is integrated out by introducing solvent-averaged interactions (PMFs) between the remaining particles. Precisely, this approach was recently used to study behavior of a common cationic surfactant *n*−decyltrimethylammonium chloride (DTMAC) in water.[8] To this end, MD simulations were used to obtain water-mediated PMFs for all pairs of constituents, that is, charged heads (modeled as tetramethylammonium ion or TMA), segment tails (modeled as $CH_4$ or ME), and $Cl^-$ counterions (CI). Given that a closely related surfactant was successfully employed to disperse CNTs in water,[9] it would be advantageous to incorporate the available simulated solvent-averaged potentials[8] into a statistical mechanical framework in order to compute the CNT−CNT PMF in an aqueous solution of DTMAC. This is the approach we take in the present work.

The desired PMF is completely determined by the surfactant density induced by two CNTs, which we compute from classical density functional theory. The details of the theory have been well documented[10] and are discussed in detail in our recent study of the interaction between nanoparticles in a solution of polymer chains.[11] Here, we simply focus on the novel features specific for the nanotube/surfactant system. In the general spirit of DFT, the equilibrium density profiles for all the constituents (TMA, ME, and CI) in an external field created by two CNTs are obtained by minimizing the grand free energy functional. The corresponding Helmholtz free energy is split into ideal and excess parts, with the latter further decomposed into hard-core and soft-tail terms. We obtain the former from the hard sphere heterochain fluid equation of state,[12] while the latter is treated within mean-field approximation;[13] the required split of PMFs into hard-core and soft-tail parts is performed according to Barker−Henderson prescription[14] (all the details are provided in the Supporting Information). The effective interactions between SWCNTs and various components in solution (needed to construct the external field) are obtained from MD simulations, as detailed in the Supporting Information.

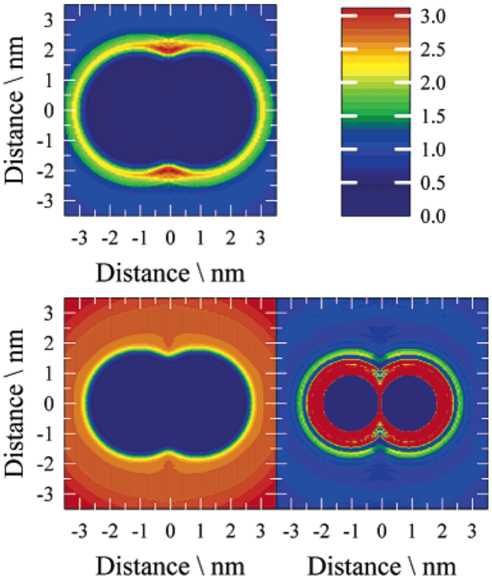

***Figure 1.*** Contour plots of the scaled density profiles. (Top left) Head Segments. (Bottom left) Counterions. (Bottom right) Tail Segments. Note: The contour plot of the counterion segments is shown using a scale of 0−1 (not 0−3) due to the lack of pronounced structure. All profiles have been scaled by their bulk density value.

Our microscopic model consists of two parallel, infinite single wall CNTs, each of diameter ~1.2 nm, immersed in DTMAC solution with concentration $\rho = 0.015$ g/cm$^3$, which is just below the CMC. The latter choice is justified by the experimental observation that stable CNT dispersions can be prepared at surfactant concentrations below CMC.[1] By working at these conditions, we can treat surfactant density profile away from CNTs as uniform, that is, we need not consider micelle formation *in the bulk*. Note, however, that cylindrical micelles with CNT as the core can still be formed even below bulk CMC.[1]

Given that both possible surfactant arrangements (cylindrical micelles and random absorption) yield *z*-independent density profiles, the latter are computed on an $(r,\theta)$ grid (see Supporting Information). In Figure 1, we present equilibrium density profiles for the head (upper left), counterion (lower left), and the tail (lower right) segments around two CNTs separated 2.05 nm. One sees that hydrophilic TMA heads are primarily located away from the

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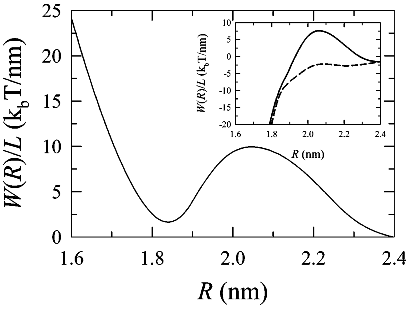

***Figure 2.*** Potential of mean force. Main: Surfactant mediated PMF. Inset: Total and tube−tube PMFs are plotted with solid and dashed lines, respectively. See text for a full description of the system.

CNT surfaces, while hydrophobic tail segments are strongly aggregated near these surfaces, in the region of the minimum of the CNT−ME PMF, whose depth is ∼2400 K (see Supporting Information). Furthermore, the width of the density profile of the tail segments (between CNT surface and peak of the head profile) is about 1 nm. This indicates that the surfactant tails are not strongly extended into the bulk (as would have been the case for cylindrical micelles), but rather are randomly arranged on the CNT surfaces, which is in agreement with structural analysis of the results of recent SANS experiments.[2] As for the counterions, they are largely located outside of the maximum of the head distribution, and their density profile does not show any pronounced structure (Figure 1).

Next, we computed the surfactant density profiles over a range of CNT separations, from which it is straightforward to obtain the surfactant-induced component of the CNT−CNT PMF;[11] the corresponding result is shown in Figure 2 (the CI-induced component is negligible). The inset of Figure 2 displays the *total* PMF, which we obtained by combining the surfactant-induced term with the PMF between two CNTs in water, as given by MD simulations of Walther et al.[15] Of primary importance is the presence of a repulsive barrier around $R \cong 2$ nm, whose height ($\approx 10\ k_BT$/nm) should be sufficient to stabilize the CNT dispersion against flocculation.[5] The general behavior of the total PMF is quite similar to the case of CNTs sterically stabilized with grafted polymer,[5] that is, a deep van der Waals minimum followed by a repulsive barrier. At the same time, the surfactant-induced component displays more structure compared to the term induced by grafted stabilizing chains.[5] While the latter monotonically becomes more repulsive with decreasing CNT separation,[5] the former passes through a pronounced minimum around $R \cong 1.85$ nm, which is followed by increasingly steep repulsion at smaller $R$. The features observed in the surfactant-induced PMF can be rationalized as follows. As the two SWCNTs with adsorbed surfactants are brought closer together from a large separation, the two respective layers of like-charged TMA heads start repelling each other, which produces a repulsive barrier around $R \cong 2$ nm. As the CNT separation is further reduced, one reaches the point where the TMA heads can no longer fit between the two tubes. At the same time, the tail segments find themselves in an energetically favorable position, as they experience a strong attraction to both tubes. This creates a "bridging attraction",[16] which manifests itself in a minimum observed around $R \cong 1.85$ nm. Finally, at even shorter separations, bridging attraction gives way to steric repulsion.[16]

In summary, we employed classical DFT to study surfactant-stabilized aqueous dispersions of CNTs. The computed density profiles indicate random adsorption of surfactants on CNT surfaces (rather than formation of cylindrical micelles), which agrees with recent SANS experiments.[2] Similar to mean-field study of sterically stabilized CNTs,[5] we observe a pronounced repulsive barrier in the CNT−CNT PMF, which is sufficient to stabilize the CNT dispersion even at bulk surfactant concentrations below the CMC value, again in agreement with experiments.[1] Future work will address the effectiveness of different surfactants.

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**Supporting Information Available:** Simulation details, theoretical details, data fitting of PMFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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