

Supplementary Data

Order-disorder transition induced by surfactant micelles in single - walled carbon nanotubes dispersions

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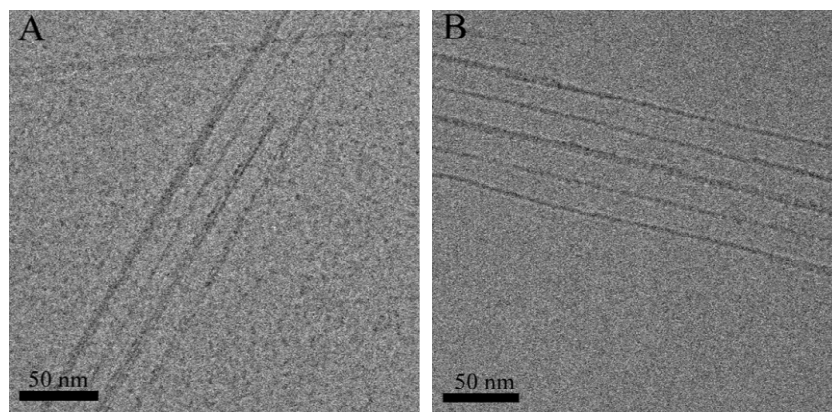


Fig. S1. Cryo-TEM images of SWNT (1 wt%) dispersed in aqueous solutions of A) 5wt% SDS showing a mean inter-tube spacing of 19nm and B) 2wt% CTAC mean inter-tube spacing of 16nm.

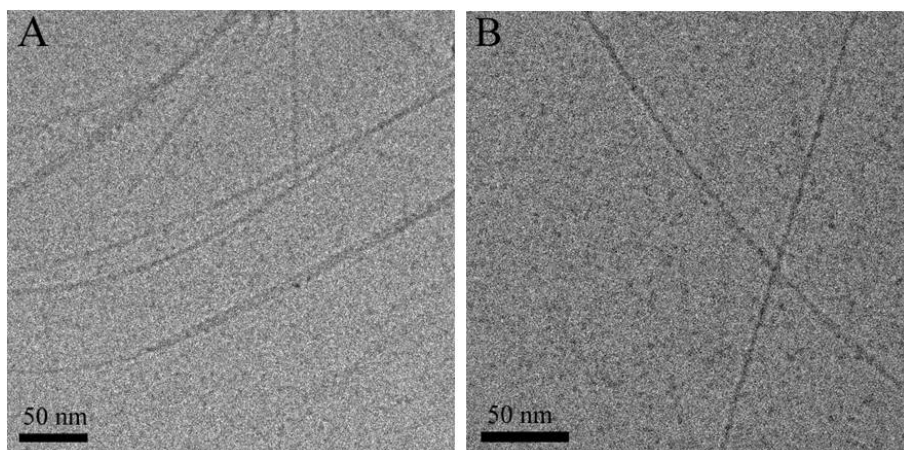


Fig. S2. Cryo-TEM images of SWNT (1 wt%) dispersed in non-ionic surfactants A) 3wt% Brij-78 and B) 3wt% triton x-100.

Table S1: Characteristics of the surfactants used in this study

Surfactant	cmc (water, 25 °C) [M]	Ordered liquid crystalline phase of surfactant micelles (water, 25 °C) [M]
CTAB $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+\text{Br}^-$	9×10^{-4}	0.6
CTAC $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+\text{Cl}^-$	1.5×10^{-3}	1.25
SDS $\text{C}_{12}\text{H}_{25}\text{SO}_4^- \text{Na}^+$	8×10^{-3}	1.4
Triton 100 $\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_{10}$	2×10^{-4}	
Brij-78 (Polyoxyethyleneglycol dodecyl ether)	4.8×10^{-5}	

Table S2: Inter-tube spacing as calculated from cryo-TEM images of CTAB dispersions.

	CTAB con. [wt%]	Inter-tube spacing [nm]
SWNT	2	26 ± 3.3
	4	19 ± 2.3
	5	18 ± 1.9
	6	17 ± 2.0
	7	16 ± 2.1
	8	16 ± 2.1
DWNT	2	24 ± 3.2
	5	19 ± 2.5
	10	16 ± 2.7

Shear effect

The preparation process of ultra-thin films for cryo-TEM involves a step of blotting that subjects the specimens to high shear rates ($\sim 10^3$ - 10^6 s^{-1})^{1,2}. The flow fields that develop during shearing may cause alignment of structures in the liquid specimen prior to vitrification of the sample. In such cases the non-perturbed structure may be restored during a relaxation period of some tens of seconds. To test the effect of relaxation on the structures presented here we performed a series of on-the-grid relaxation experiments where the samples were incubated for up to 100 seconds in a controlled environment, prior to quench-cooling. Statistical analysis of cryo-TEM images is presented in Fig. S3. The data suggest that the orientational ordering and the

inter-tube spacing between the co-aligned SWNT are preserved. We note as well that that the number of co-aligned tubes is not modified by the relaxation.

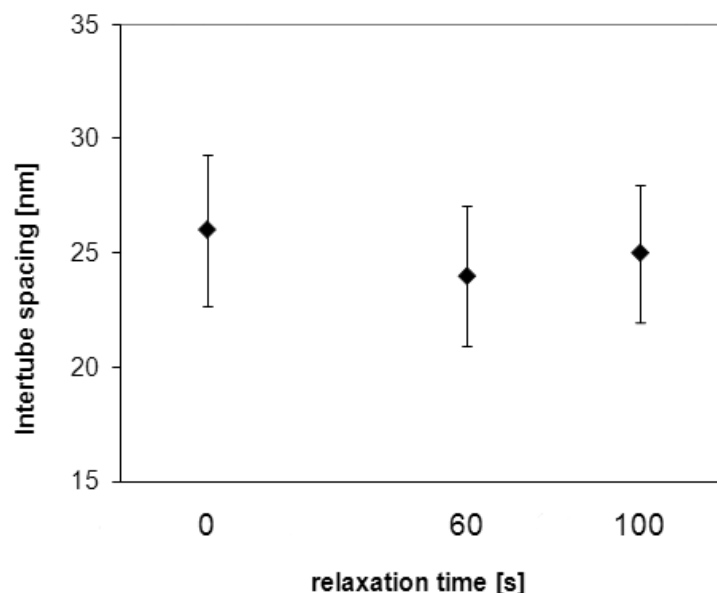
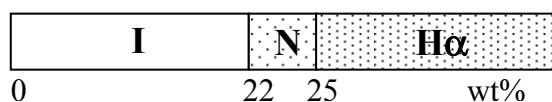


Fig. S3. Inter-tube spacing as a function of relaxation time.



Scheme 1: The phase diagram of CTAB at 25 °C (cmc = 0.03 wt%) , showing the transition from isotropic (I) to nematic (N) to hexagonal(H α) (16).

Theoretical approach

Fig. S4 (left) shows the free energy, effective interaction, between two parallel nanotubes of 1nm diameter. The conditions are for the case in which there is a small concentration of CTAB micelles in the solution. The predictions show that the interactions are purely repulsive and the strength of the repulsion increase with decreasing salt concentration, a signature of electrostatic dominated interactions. Fig. S4 (right) shows the effective interactions when the concentration of micelles is larger

and it is in the range of the experimental results. A clear oscillatory attraction appears. These attractions arise from the depletion interactions. Note that in contradiction to the experimental observations, the strength of the attractions increases as the salt concentration increases, opposite to the behavior observed experimentally.

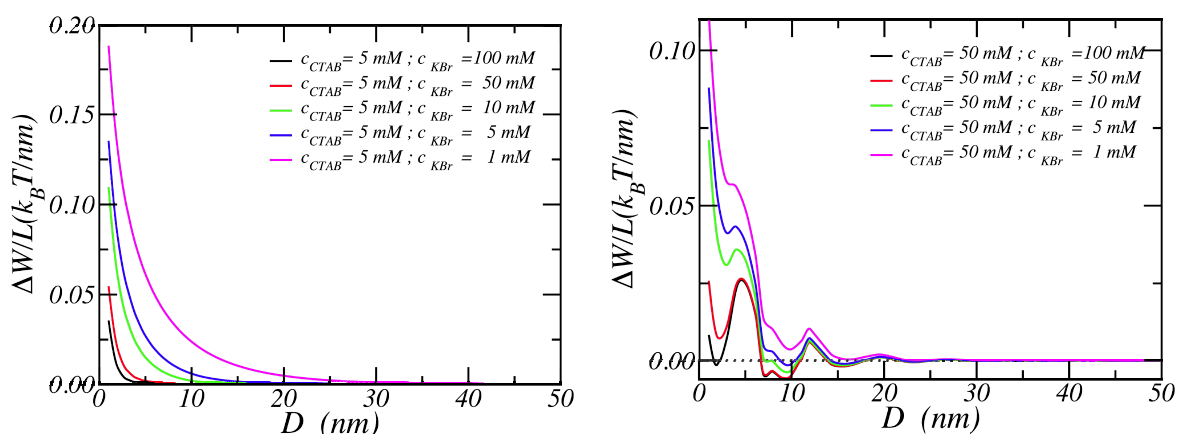


Fig. S4: The effective interactions, free energy per unit length, between two parallel CNT coated with charged surfactants in the presence of micellar surfactants and added salt. The label shows the different conditions. Left low micellar concentration, right high micellar concentration. The charge density of the CNT and the micelles is 0.25 e/nm and 0.127 e/nm^2 respectively.

In the following we present an outline of molecular theory employed to compute the effective interactions between two parallel oriented CNTs coated with charged surfactants in the presence of micellar surfactants and added salt. The theoretical approach explicitly incorporates the molecular details of each species in the system treated. Hence, the size, shape, conformation, and charge distribution of every molecule type is accounted for exactly. The theory has originally been developed to describe various interfacial polymer systems^{3,4} and recently extended to study the dispersion of polymer coated carbon nanotubes⁵⁻⁷ and the behavior of weak polyelectrolytes tethered to planar and cylindrical surfaces⁶. For more details on the theoretical derivation and examples on the ability of the theory to properly predict the

behavior of related experimental polymeric systems, see the reviews refs^{3,4,8} and references therein.

Consider two parallel oriented cylinders (CNT) of length L and radius R positioned a distance D apart in an aqueous solution. The solution contains large charged micellar surfactants of CTAB and added salt, which have a concentration of c_{CTAB} and c_{KBr} respectively. The potassium bromide (KBr) is assumed to be fully dissociated. The counter ion of the CTAB micelles is considered to be the bromide ion.

For a long CNT, $L \gg R$, we can ignore end effects of the nanotube and assume that the system is homogeneous in the direction parallel to the CNT. The free energy per unit length of the nanotube is then given by

$$\begin{aligned} \frac{\beta W(D)}{L} = & \int dx dy \rho_M(x,y) (\ln \rho_M(x,y) v_w - 1 \beta \mu_M) + \\ & \int dx dy \rho_{K^+}(x,y) (\ln \rho_{K^+}(x,y) v_w - \beta \mu_{K^+}) + \int dx dy \rho_{Br^-}(x,y) (\ln \rho_{Br^-}(x,y) v_w - 1 - \beta \mu_{Br^-}) + \\ & \int dx dy \rho_w(x,y) (\ln \rho_w(x,y) v_w - 1) + \\ & \beta \int dx dy \left(\rho_q(x,y) \psi(x,y) - \frac{1}{2} \epsilon_w (\nabla \psi(x,y))^2 \right) + \beta \int dx dy \phi_M(x,y) U_{\text{CNT}}(x,y) + \\ & \beta \int dx dy \pi(x,y) (\phi_M(x,y) + \phi_{\text{CNT}}(x,y) + \phi_{K^+}(x,y) + \phi_{Br^-}(x,y) + \phi_w(x,y) - 1) \end{aligned} \quad (1)$$

The first three terms in the free energy correspond to the mixing entropy and chemical potential of the CTAB micelle (M), the cation (K^+), and anion (Br^-) respectively. Observe that the integrals extend over the xy plane, which is perpendicular to the axis of the CNT. The next term in the free energy corresponds to the mixing entropy of the water. Here $\rho_i(x,y)$ denotes the density of component i at position (x,y) and v_w is the volume of one water molecule. The fifth term in the free energy describes the electrostatic contribution to the free energy⁹. Here $\psi(x,y)$ is the electrostatic potential and $\rho_q(x,y)$ is the total charge density, which is given by

$$\rho_q(x,y) = \rho_{CNT}(x,y) + \rho_{q,M}(x,y) + e\rho_{K^+}(x,y) - e\rho_{Br^-}(x,y) \quad (2)$$

The first two terms corresponds to the charge density of the CNT and micelles respectively, while the last two terms in the total charge density correspond to the charge density of the cation and anion.

The sixth term in the free energy correspond to a potential ensuring that the micelles cannot penetrate the nanotube. The other ions and solvent molecules are allowed to penetrate the nanotube. The micelles, because of their size, are excluded from the inside of the nanotube. The functional form of the potential is $U_{CNT}(x,y) = 0$ if (x,y) is outside of the nanotube and ∞ if (x,y) is located inside of the nanotube. Here $\phi_M(x,y)$ corresponds to the volume fraction of the micelle. For the small molecular ions and the water the volume fraction is simply related to the density of the molecules by: $\phi_i(x,y) = \rho_i(x,y)v_i$, where v_i is the size of the molecule ($v_w = 0.03 \text{ nm}^3$, $v_{K^+} = 0.011 \text{ nm}^3$, and $v_{Br^-} = 0.032 \text{ nm}^3$). However for the large micelles we need to take into account its spatial extend. This is done by relating the volume fraction of the micelle to the density in following way^{4,10,11}

$$\phi_M(x,y) = \int dx' dy' \rho_M(x,y) v_M(x,y;x',y') \quad (3)$$

where $v_M(x,y;x',y') dx' dy'$ corresponds to the volume that the micelle located at (x',y') contributes at position (x,y) . In a completely equivalent we define the charge distribution of the micelle

$$\rho_{q,M}(x,y) = \int dx' dy' \rho_M(x,y) q_M(x,y;x',y') \quad (4)$$

Here $q_M(x,y;x',y')dx'dy'$ is the charge that the micelle located at (x',y') contributes at position (x,y) . The volume distribution v_M can be relatively easily obtained through a Monte Carlo integration. We assume that micelle has a spherical shape of diameter $D_M=2.5$ nm, which correspond to an aggregation number of around 100 surfactants. For the charge distribution we assume that 10% of the surfactants are charged. The charges are uniformly distributed in the “outer layer” of the micelle. The thickness of the layer or shell is equal to $\delta=0.16$ nm (the numerical discretization in the x and y direction). In a similar fashion charge and volume is distributed on the CNT.

Finally, the last term in the free energy describes the intermolecular excluded volume interactions between all molecules. They are accounted by assuming that the system is incompressible. These packing constraints are enforced through the introduction of the Lagrange multipliers $\pi(x,y)$, which physical, correspond to the position dependent lateral pressures 3.

Minimization of the free energy with respect to the densities leads to following equations for micellar, ionic, and solvent densities.

$$\begin{aligned}\rho_M(x,y)v_w &= \exp(-\beta\mu_M)\exp(-\beta\int dx'dy'[\pi(x',y')+U_{CNT}(x',y')])v_M(x',y';x,y)+\psi(x',y')q_M(x',y';x,y)] \\ \rho_i(x,y)v_w &= \exp(-\beta\mu_i)\exp(-\beta\pi(x,y)v_i-\beta\psi(x,y)q_i) \\ \rho_w(x,y)v_w &= \exp(-\beta\pi(x,y)v_w)\end{aligned}\tag{5}$$

Functional variation with respect to the electrostatic potential $\psi(x,y)$ results in the Poisson equation.

The functional minimization of the free energy yields a set of non-linear equations which depends on the lateral pressures $\pi(x,y)$ and on the electrostatic potential $\psi(x,y)$. The application of the theory requires the determination of the lateral pressures and electrostatic potential. Technical details of how to apply and numerical

solve the theory can be found in refs^{3,8}. The input necessary to solve the theory are the size, shape, and charge of the molecular species, and the composition of the bulk aqueous solution, i.e., the micelle and salt concentration. The theory then will provide us with any thermodynamic and structural quantity of the system. Most importantly, we will be able to calculate the free energy versus the separation of CNTs.

References

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