

## Dispersion of Carbon Nanotubes in Aqueous Solutions of Ionic Surfactants

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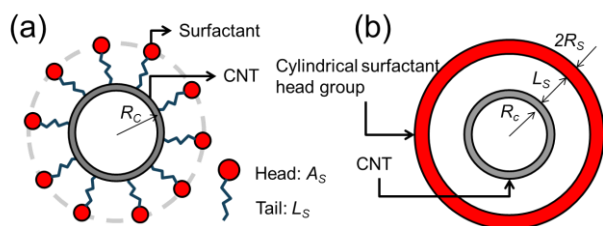
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In this work, we present a mean-density model of surfactants to illuminate the mechanism of carbon nanotube (CNT) dispersion in aqueous solutions of ionic surfactants. Ionic surfactants have been widely used to make well-dispersed aqueous CNT suspensions. However, the mechanism of the dispersion is not clear. [1] To understand the mechanism, molecular dynamics (MD) simulations were recently employed, but they require high computing power to obtain significant results. [2, 3] With the mean-density model, we can effectively estimate the mean force potential between CNTs stabilized with surfactants. Notably, we find that the osmotic pressure between CNTs plays an important role in the suspension stability. The mean-density model can help to determine appropriate surfactants and concentrations necessary for stable CNT dispersions.

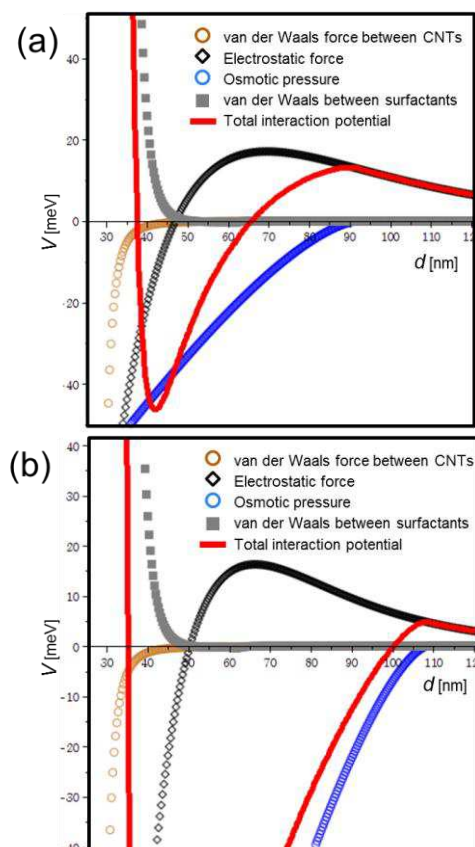
In the mean-density model, the surfactant heads suspended on a CNT are assumed to constitute a single cylindrical group. When a CNT is dispersed in aqueous solutions with ionic surfactants, the surfactant tails are attached to the CNT due to its hydrophobicity. However, the hydrophilic heads of the surfactants orient towards the water (figure 1(a)). If we assume that the surfactants are attached on the CNT surface uniformly, the CNT and surfactant assembly can be simplified as shown in Figure 1(b). In the mean-density model, there are two cylindrical groups corresponding to the surfactant head and the CNT. The CNT has uniform carbon atom density, resulting in the same weight as the actual CNT. Similarly, the surfactant head group has uniform density and valence charge.



**Figure 1.** Schematic illustrations of carbon nanotube and surfactant assemblies. The surfactant is composed of a hydrophilic head, which has the cross sectional area of  $A_s$  (the head radius is  $R_s$ ) and a hydrophobic tail, which has length  $L_s$ . (a) In reality, multiple surfactants are attached on the surface of the CNT. (b) In the simplified model, the surfactant heads are considered a single cylinder.

To verify the mean-density model, we compare the total interaction potentials obtained from our model and the molecular dynamics (MD) simulation. In our model, the total interaction potential was calculated by superposing the van der Waals force, the electrostatic force, and the osmotic pressure between two the CNT-surfactant assemblies shown in Figure 2(b). As a result, the total interaction potential obtained from the mean-density model (Figure 2(a)) agrees well with the MD simulation. [3] Furthermore, our model successfully shows the effect of surfactant concentration on dispersion stability. When the bulk solution concentration is higher than the surfactant critical micelle concentration (CMC),

micelles of the surfactant form in solution, maintaining the bulk monomer concentration at CMC. Therefore, the osmotic attraction force becomes significant when the bulk concentration is higher than CMC, lowering the maximum potential barrier, as shown in Figure 2(b). From this result, we see that the CNT dispersion is unstable when the surfactant concentration is higher than the CMC. [4]



**Figure 2.** Total interaction potentials between two CNT-surfactant assemblies. The total interaction potential can be obtained by the summation of van der Waals force, electrostatic force, and osmotic pressure. The total interaction potentials of (a) and (b) are obtained with the surfactant coverage ratio of 30 % and the tail stretching ratio of 100 %. Different bulk surfactant concentrations of CMC ( $8.7 \times 10^{-3}$  mol/L) and  $2 \times$ CMC are used in (a) and (b) to compare the effect of micelle formation

The mean-density model shows reasonable predictions for the interaction potential between CNT-surfactant assemblies with much less computational time than the molecular dynamic simulations. Furthermore, this model illuminates the effects of osmotic pressure between the assemblies on dispersion stability. This result shows that more CNT agglomerates form when the surfactant concentration is higher than the CMC, and the most stable CNT-surfactant suspension is obtained around the CMC.

## References

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