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Controlling carbon-nanotube—phospholipid solubility by curvature-dependent self-assembly

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Abstract

Control of aqueous dispersion is central in the processing and usage of nanoscale hydrophobic objects. However, selecting dispersive agents based on the size and form of the hydrophobic object and the role of coating morphology in dispersion efficiency remain important open questions. Here, the effect of the substrate and the dispersing molecule curvature, as well as, the influence of dispersant concentration on the adsorption morphology are examined by molecular simulations of graphene and carbon nanotube (CNT) substrates with phospholipids of varying curvature as the dispersing agents. Lipid spontaneous curvature is increased from close to zero (effectively cylindrical lipid) to highly positive (effectively conical lipid) by studying double tailed dipalmitoylphosphatidylcholine (DPPC) and single tailed lysophosphatidylcholine (LPC) which differ in the number of acyl chains but have identical head group. We find that lipids are good dispersion agents for both planar and curved nanoparticles and induce a dispersive barrier non-size selectively. Differences in dispersion efficiency arise from lipid head group density and their extension from the hydrophobic substrate in the adsorption morphology. We map the packing morphology contributing factors and report that the aggregate morphologies depend on the competition of interactions rising from 1) hydrophobicity driven maximization of lipid—substrate contacts and lipid self-adhesion, 2) tail bending energy cost, 3) preferential alignment along the graphitic substrate principal axes, and 4) lipid head group preferential packing. Curved substrates adjust the morphology by changing the balance between the interaction strengths. Jointly, the findings show substrate curvature and dimensions are a way to tune lipid adsorption to desired, self-assembling patterns. Besides engineering dispersion efficiency, the findings could bear significance in designing materials with defined molecular scale, molecular coatings for orientation specific CNT assembly or lipid-based molecular masks and patterning on graphene.

Introduction

Nanomaterials have unique chemical, biological and physical properties compared to the same substances in bulk. In particular, carbon nanotubes (CNTs) possess excellent tensile strength, extraordinary thermal conductivity, and interesting electronic structure offering unique opportunities for a wide range of applications from electronics, optics, and reinforcement of composites to biochemical sensing devices and antimicrobial agents.¹⁻³ In aqueous solution, CNTs bundle strongly together by hydrophobicity. Yet, realizing their extraordinary properties for the applications often requires dispersions of pure and well-isolated CNTs. Such CNT dispersion in aqueous environment can be achieved by covalent hydrophilic or non-covalent amphiphilic functionalization, see, e.g., Refs.⁴⁻⁶ Non-covalent functionalization, e.g., polymers, surfactants, and lipids, is often preferred as it maintains the individual CNT structure, and properties intact. In general, in non-covalent functionalization of CNTs, the hydrophobic interactions between the solvating molecule and the graphitic surface induce adsorption, while the hydrophilic sections provide effective repulsion against rebundling which stabilizes the aqueous dispersion.^{7,8} For polymers, this repulsion rises dominantly from steric interactions but for small amphiphiles, the topic is more complicated with Coulombic repulsion (for ionic species) and hydration contributing to the barrier. In fact, the resulting CNT solubility has been reported to be dispersing surfactant species dependent (for reviews, see Refs.^{6,7}) but also heavily dependent on surfactant concentration^{9,10} and CNT diameter, with narrow CNTs more easily stabilized than wider ones.^{11,12} In particular, Clark *et al.* have studied multi-walled CNT dispersion by several ionic and non-ionic surfactants reporting surfactant concentration dependent solubility with the solubility reaching a saturation level at high enough, surfactant dependent concentration.⁹ In Ref.¹⁰ surfactant concentrations for dispersion of CNTs are optimized.

In addition, a number of experimental studies have addressed surfactant and lipid adsorption and morphologies on graphite¹³⁻¹⁵ and CNTs¹⁶⁻¹⁹ in aqueous environment. For planar graphite, calorimetric studies by Király *et al.* show anionic sodium n-decyl sulfate

forms at low concentrations a flat, monomolecular layer ordered on the graphite surface.¹³ At higher concentrations, the ordered monolayer guides the formation of hemimicellar aggregates.¹³ For nonionic surfactants, the calorimetric studies by Király and Findenegg¹⁴ on planar graphite and the AFM study of SDS on graphite oxide by Glover *et al.*¹⁵ suggest also hemi-cylindrical aggregates. On the other hand, on multi-walled CNTs, single-tailed ionic surfactants have been reported to form helical striations.^{16,17} Also on multi-walled CNTs, Richard *et al.* speculated that the various helical striations they observed SDS to produce follow the underlying carbon network.¹⁶ Furthermore, single-tailed lipids, such as lysophosphatidylcholine (LPC) and lysophosphatidylglycerol have been also found to form striations on CNTs.¹⁸

Although the experimental works show both the adsorption morphologies and the solubility are surfactant, surfactant concentration, and substrate curvature dependent, the specific relation of the adsorption morphology to surface curvature (particle size) and the resulting solubility efficiency remain challenging to probe experimentally because of the aqueous environment and the soft, non-crystalline, and dynamic aggregates. On the other hand, computer simulations allow detailed probing of the aggregates and their dynamics at these aqueous interfaces. Thereby, various simulational studies of both single-²⁰ and double-tailed lipids,^{21,22} as well as, surfactants^{23–28} on CNT and graphitic surfaces in aqueous environment have been carried out in atomistic detail. More coarse-grained molecular modelling studies for both single tailed LPC²⁹ and its double tailed equivalent dipalmitoylphosphatidylcholine (DPPC)^{29–32} exist. Additionally, surfactant self-assembly on CNTs has been studied on the dissipative particle dynamics (DPD) level, which omits the specific chemical detail of the molecules, see e.g. Refs.^{33–35}

The main focus in the prior simulational studies has been on characterizing the adsorbed structures and dynamics based on surfactant type with Refs.^{29,32} presenting comprehensive studies on LPC and DPPC and Ref.³⁶ studying adsorption as a function of induced membrane curvature. However to our knowledge, the role of curvature is addressed only by the atomistic

simulations studies by Tummala *et al.* for ionic SDS^{23,37} and flavin mononucleotide (FMN),²⁵ and Suttipong *et al.* for SDS³⁸ and SDBS,²⁴ as well as, the theoretical level examinations and lattice Monte Carlo simulations by Tian *et al.*³⁹ The current work assesses the role of both substrate- and dispersing lipid curvatures on adsorption behavior and interactions on molecular level, as well as, takes the examination to the level of dispersion efficiency.

Here, we examine the effect of substrate and solvating molecule curvature on amphiphile adsorption and aggregate morphologies, as well as, the resulting aqueous dispersion efficiency by molecular simulations. In particular, we study phospholipid interactions at planar graphite and curved CNT surfaces. Zwitterionic phospholipids are chosen as the model system as lipids have been used for efficient CNT dispersion in, e.g., Refs.^{12,18,19,40,41} The two lipids studied here, DPPC and LPC, differ only in the number of hydrocarbon tails. In aqueous solution, they form planar bilayers (DPPC) or spherical micelles (LPC) due to their shape (molecular spontaneous curvature). This allows us to study systematically the effect of molecular and substrate curvature in amphiphile adsorption and the resulting CNT dispersion.

Methods

Atomistic simulations

Parameters for the all-atom description of the DPPC were taken directly from the CHARMM36 lipid force field.⁴² LPC was constructed from DPPC by replacing the *sn-2* lipid tail with a hydroxyl (OH) group. The OH group parameters are those of CHARMM27 phosphoglycerol residue.⁴³ The OH partial charges were re-scaled to $q_O = 0.66e$ and $q_H = 0.50e$ to match the CHARMM36 partial charge modifications, where the dipole moment of the lipid carbonyl group was increased compared to CHARMM27. Carbon atoms in graphene and CNTs were modelled with the atom type CA using 0.142 nm as the carbon-carbon bond length. To maintain also the largest CNTs in form, the improper dihedral harmonic potentials between

the CA atoms were given an artificially high force constant of $1500 \text{ kJ mol}^{-1} \text{ rad}^{-2}$. The water model is the CHARMM modified TIP3P water model,⁴⁴ which has Lennard-Jones interactions also for the hydrogen atoms. This water model was chosen as it was used in the parameterization of the CHARMM36 lipids⁴² and is the recommended⁴⁵ water model for CHARMM36 lipid simulations.

Long-range electrostatic interactions in the atomistic simulations were calculated using the PME method,⁴⁶ with a sixth-order smoothing spline. A real space cut-off of 1.2 nm was employed while the simulation package was allowed to determine the optimal grid spacing in the reciprocal space. Lennard-Jones potentials were smoothly shifted to zero between 0.8 nm and 1.2 nm. No long range dispersion correction was applied. Bonds involving hydrogen were constrained using the LINCS algorithm.⁴⁷ Equations of motion were integrated with the leap-frog algorithm using a time step of 2 fs. Similar simulation parameters have been recommended to be used with the CHARMM36 force-field and GROMACS by Piggot *et al.*⁴⁵ The stochastic velocity rescaling thermostat of Bussi *et al.*⁴⁸ was used with reference temperature of 325 K and a relaxation time constant of 0.5 ps. Water, lipids, and the carbon substrate were coupled separately to the heat bath. Pressure was kept constant using a semi-isotropic Parinello-Rahman barostat⁴⁹ with a time constant of 4.0 ps. In the simulations, the center of mass motion was removed separately for the graphite surface/CNT and the aqueous solution including the lipids.

Coarse-grained simulations

The MARTINI force-field used in the study for the coarse-grained (CG) simulations is originally developed for lipids and detergents,^{50,51} but later extended to also proteins,⁵² lipoproteins,⁵³ fullerenes,^{54,55} graphene⁵⁶ and CNTs²⁹ as well as bio- and synthetic polymers, such as PL-PEG^{57,58} and polystyrene.^{59,60} In the MARTINI model, the molecule is described by specific interaction centers: on average one interaction center describes four non-hydrogen atoms. Such coarse-graining of the interactions allows us to study larger systems and longer

timescales with the same computational effort than in full atomistic detail. This enables studying lipid-CNT complex at higher concentrations where the lipid aggregate relaxation times are prohibitive of the use of full atomistic detail model. The speed-up is mainly due to the CG approach smoothing out the interaction potential enabling the use of a longer time-step. Additionally, due to the smoothing of the interaction potential, the CG simulation time corresponds to a significantly longer actual time. For MARTINI, a factor of 4 based on, e.g., diffusion rates is typically used in converting the simulation time to real time.^{51,61} In this work we have not converted the simulation times.

The CG CNT models were coarse-grained as described previously.⁶² This model uses 3-to-1 mapping with a CG bead-to-bead distance of 2.84 Å (the atomistic carbon-carbon separation is 1.42 Å) and preserves chirality and symmetries of the atomistic detail CNT. Due to the large curvature frustrations in the thinnest CG tubes, the CG CNT bead distances are constrained by the LINCS algorithm.⁴⁷ For CG water and lipids, standard MARTINI water and DPPC and LPC lipid models beads were used, see Figure 1. The CNT interaction model and the force constants of the CNT beads are described in Ref.²⁹ A cut-off of 1.2 nm was employed for the Lennard-Jones and electrostatic interactions. The Lennard-Jones interactions were shifted to zero smoothly between 0.9 nm and 1.2 nm, and the Coulombic interactions between 0 nm and 1.2 nm. A time step of 20 fs was used. Also the CG simulations were performed in NPT ensemble. As with the atomistic simulations, the stochastic velocity rescaling thermostat of Bussi *et al.* was employed⁴⁸ with temperature $T = 298$ K. A pressure of 1 bar was maintained with the Parrinello-Rahman pressure control⁴⁹ using a time constant $\tau_p = 24$ ps semi-isotropically with the CNT axial direction pressure controlled separately. With the exception of a larger time constant for pressure control which was applied to prevent rapid pressure changes along the CNT axial direction, the setup corresponds to the standard MARTINI simulation protocol.

Simulation configuration details and preparation

The details of all simulated systems are summarized in Table 1. In all simulations of this work, periodic boundary conditions were applied. In the atomistic simulations, planar graphite surface of size $6.39 \times 6.15 \times 6.00 \text{ nm}^3$ and CNTs of length 12.778 nm with lipid coverage close to a monolayer were studied. This corresponds to 16 – 80 lipids on (10,0), (18,0), and (36,0) CNTs. These CNT wrapping indices correspond to CNT diameters of approximately 0.8 nm, 1.4 nm, and 2.8 nm. To isolate the influence of the head group and crowding, hexadecane (HD) (the corresponding alkyl chains without the lipid head group) monolayers and a sparse, two lipid coverage were examined. The atomistic simulations were run for 75 ns (lipids) or 20 ns (HD) with 35 ns (lipids) and 5 ns (HD) disregarded in the analysis as initial relaxation period. The relaxation time was determined from stabilization and uniformity of the adsorbed surfactant coating.

In the CG simulations, a simulation box of size $21 \times 21 \times 41 \text{ nm}^3$ with the CNTs spanning the box in its longest dimension was considered. (10,0) and (18,0) CNTs which with the 3-to-1 CG mapping result into CG (5,0) and (9,0) nanotube models were studied by the CG simulations. The CG systems contain 800 LPC or DPPC molecules (w/v ratios of 41.2 g/L for LPC and 69.4 g/L for DPPC) which are free to adsorb, desorb and form micelles in the aqueous phase. In the simulations, DPPC has a higher w/v concentration than LPC to accelerate dynamics so that a full coating was achieved within simulation timescales. The CG systems are solvated with ≈ 135000 CG water molecules. The last 400 ns of the $4\mu\text{s}$ CG simulation is used for analysis; the CG systems in this work, despite the extensive simulation time and although stabilized in morphology and aggregation number, are only approaching equilibrium, and complete coating.

The starting structures for the graphite surface and CNTs for both atomistic and CG simulations were constructed using the Atomistic Simulation Environment.⁶³ Initial simulation configurations were generated by placing lipids randomly in the simulation box with lipid positioning restricted to outside of the CNTs in the CNT simulations or to distances

less than 4.0 nm above the graphite plane (to ensure all lipids adsorb on the same side of the graphite plane). No water was allowed inside the CNTs. The steepest descent method was utilized to minimize the initial configurations in energy.

Umbrella sampling simulations were performed to assess the dispersive effectivity of the lipid coating. These simulations employed a fully coated CNT segment from the CG simulations (CNT segment length halved from that of the CG simulation CNT length to reduce computational cost). The tube segment was duplicated and the two coated CNTs were placed perpendicular to each other 10 nm apart. The perpendicular orientation of the CNTs during the simulation is maintained by the periodicity of the rectangular simulation box which enforces the CNTs to remain aligned parallel to box lattice vectors and perpendicular to each other in the box. We also note that the 90° angle is the theoretically optimal angle for calculating the free energies between two repulsive cylinders as it gives the minimal (point-like) contact area and eliminates torque regardless of the cylinder length. A total of 100 sampling windows was generated at 0.1 nm intervals by pulling the CNTs together with constant rate of 0.6 nm ns^{-1} . The sampling windows configurations corresponding to intertube distances of less than 7.5 nm were employed for the umbrella sampling simulations (a total of 75 configurations). The distance restraints were applied by using a force constant of $3000 \text{ kJ mol}^{-1} \text{ nm}^{-2}$ for the harmonic umbrella potential and the force acting on the constraint was recorded every 2 ps. Each umbrella window was simulated for 100 ns of which the first 40 ns was disregarded in the analysis. The bias potentials from the umbrella windows were removed with the weighted histogram analysis method (WHAM).^{64,65} The simulated potentials of mean force contain statistical uncertainty due to restrictions in the extent of sampling.

Table 1: Summary of simulated lipid systems.

Substrate	Lipid	Box size (nm ³)	Number of lipids	Final coverage (lipids/nm ²)
graphite (planar)	DPPC	$6.39 \times 6.149 \times 6.0$	2	0.05
(36, 0) CNT	DPPC	$7.4 \times 7.4 \times 6.389$	2	0.02
(18, 0) CNT	DPPC	$6.0 \times 6.0 \times 6.389$	2	0.05
(10, 0) CNT	DPPC	$6.0 \times 6.0 \times 6.389$	2	0.07
graphite (planar)	LPC	$6.39 \times 6.149 \times 6.0$	2	0.05
(36, 0) CNT	LPC	$7.4 \times 7.4 \times 6.389$	2	0.02
(18, 0) CNT	LPC	$6.0 \times 6.0 \times 6.389$	2	0.05
(10, 0) CNT	LPC	$6.0 \times 6.0 \times 6.389$	2	0.07
graphite (planar)	DPPC	$6.39 \times 6.149 \times 6.0$	16	0.41
(36, 0) CNT	DPPC	$7.4 \times 7.4 \times 12.776$	54	0.39
(18, 0) CNT	DPPC	$6.0 \times 6.0 \times 12.776$	32	0.40
(10, 0) CNT	DPPC	$6.0 \times 6.0 \times 12.776$	22	0.40
graphite (planar)	LPC	$6.39 \times 6.149 \times 6.0$	24	0.61
(36, 0) CNT	LPC	$7.4 \times 7.4 \times 12.776$	80	0.58
(18, 0) CNT	LPC	$6.0 \times 6.0 \times 12.776$	47	0.58
(10, 0) CNT	LPC	$6.0 \times 6.0 \times 12.776$	33	0.60
CG (18, 0) CNT	DPPC	$21.0 \times 21.0 \times 40.896$	800	2.24
CG (10, 0) CNT	DPPC	$21.0 \times 21.0 \times 40.896$	800	3.35
CG (18, 0) CNT	LPC	$21.0 \times 21.0 \times 40.896$	800	1.61
CG (10, 0) CNT	LPC	$21.0 \times 21.0 \times 40.896$	800	2.40

Figure 1: At left, the structures of the studied molecules and their coarse-grained representations. The color coding shows the MARTINI bead types used to represent the coarse-grained molecules. At right, a sample initial simulation configuration showing a (36,0) CNT with 54 DPPC lipids.

Results

In the simulations, the lipids readily adsorb to all graphitic surfaces due to the hydrophobic effect, *i.e.*, the surface tension difference between the substrate and water is greater than that of water and the lipid tails. While some lipids adsorb directly, most form small aggregates which then adsorb. This is expected based on the critical micelle concentrations (CMC) which are 0.46 nM for DPPC and 0.4 μ M for LPC.⁶⁶

The simulation snapshots of Figure 2 shows lipid tails pack tightly parallel or antiparallel to each other forming a flat monolayer of patches on the planar graphene substrate. This results from the very strong lipid tail-tail adhesion. The patches appear to have preferential orientation directions: the lipids orient along the lattice principal axes on planar graphene, see Figure 3 showing tail orientation distributions. The preferential orientation rises from optimization of the alkane tail—substrate contacts.⁶⁷ The orientation propensity naturally scales with the alkane chain length, so the double-tailed DPPC has a stronger preference to the graphene principal axes directions than the LPC. The orientation preference is relatively

weak compared to thermal energy⁶⁷ and arises mostly as a collective crowding effect, as indicated by LPC populating also the unfavorable orientations.

Cylindrical CNTs have a finite curvature along the radial and zero curvature on the axial direction. This means the total curvature observed by a lipid depends on its tilt-angle. Therefore, strong adhesion to a CNT induces a bending force on the alkyl chains. This is shown as kinks (or gauche defects) on the acyl chain, enabling the acyl chains to follow the substrate curvature. Figures 2 and 3 show the lipid orientation along the CNT axis. The axial preference is strongest for lipids on the thinnest CNTs. This is because thin CNTs have the highest curvature and so induce strongest bending. This indicates the energy involved in introducing gauche defects which would enable the acyl chains to follow the curvature is greater than the energy gain in following the graphene symmetry orientations, or satisfying other favorable intramolecular interactions, and axial orientation where the chains can remain straight while shielding the substrate and themselves dominates. The overall cost of bending increases with increasing curvature making the axial orientation preference stronger for the thin tubes. As before, DPPC has stronger axial orientation than LPC due to its two tails.

Even though the gauche defects are costly, and high CNT curvature clearly promotes axial lipid orientation, the number of gauche defects increases significantly with increasing substrate curvature, see Figure 4. The data in Figure 4 shows especially the (10, 0) CNT as a substrate promotes a significant increase to the number of gauche defects in comparison to planar substrate where the lipids are practically frozen; the presence of the substrate reduces the kink probability significantly from bulk aqueous solution due to reduction of degrees of freedom. Figure 4 also reveals the gauche defects are more probable at both tail ends. This is because the atoms at the tail ends are more susceptible to thermal motion. The increased gauche defect probability near the lipid ester groups is due to the asymmetric glycerol backbone conformation and lipid head group tilting away from surface. Additionally, the gauche defect probability along the hydrocarbon chain has a zig-zagging form. This results from the chain symmetry, and has been previously reported for, e.g., SDS in bulk

and at interfaces.^{27,68}

Furthermore, the lipid head group interactions influence the lipid packing on the substrate. Simulations of HD isolate this effect as they represent just the tail interactions with the substrate. Comparison of HD and the lipid data in Figure 2 shows the lipid head group interactions favor a charge-charge connected head group packing morphology. Upon decreasing curvature, ring-like bands around the CNTs transition into helical wrapping as a result from the interplay between CNT axial orientation preference, tail bending penalty, and head group-head group interactions, see Figure 2 and the highlights. In comparison, HD packs as rings and tightly packed patches (data not shown). At high curvatures, this tight patchy packing occurs even at the cost of extra gauche defects, see Figure 4; if HD were to wrap around the CNT in helices, the helical wrapping would be induced by graphene axial directions preference but the fact that the helical wrapping is lost for HD signifies a) the lipid head groups cause the helical wrapping b) the head group interactions can act to stabilize a packing morphology. Additionally, Figure 4 show a comparable amount of disorder (gauche defects) for HD as the lipids. This indicates the presence of the head group does not systematically increase the number of bends.

The two-tailed character of DPPC causes it to exhibit a wider variety of structures on the substrate than LPC. DPPC may have the lipid tails either together or separated to 180° angle in a linear conformation, see Figure 2. Lipids with intermediate conformations, such as tails oriented perpendicular to each other, are also present but in much lesser numbers, and typically only when the hydrophobic substrate would be exposed otherwise. As expected, the intermediate forms become less likely when curvature is increased due to the cost of bending. Interestingly, the lipids that have their tails separated by approximately 180° angle tend to gather into small clusters. This behaviour seems to be at least partially driven by the dipole interaction between the tail ester groups and the ionic bonding between phosphate and choline groups. Furthermore, in clusters containing multiple lipids, the oppositely charged ionic groups in neighbouring lipids form short chains. Indeed, computational

studies of PC membranes indicate that similar charge-paired strips are present also in bilayer morphology.^{69,70} The effect is more pronounced here than in bilayers because the lipids are frozen and packed in a specific order. In contrast, the charge-paired strips in fluid bilayers can occur in any direction with lipids also intermixing due to diffusion.

Figure 2: Top and side views of DPPC (left) and LPC (right) monolayers on planar graphite and curved CNT surface. DPPC forms an interconnected layer while LPC adsorbs in linear strips forming spirals on curved surface. Color highlights show aligned and spread tails forming patches, interconnected layers, and spirals around the CNTs and on graphene. Water and hydrogen atoms have been omitted in the visualization for clarity. The graphite plane and the dashed lines show the simulation cell size; periodic boundary conditions are employed.

Higher concentrations

The monolayer coverage represents either the morphology at extremely low concentration limit or the transient initial layer of lipid coating at higher concentrations. To understand the behavior of lipid-CNT complexes closer to saturated coverage conditions, we also per-

Figure 3: DPPC, LPC, and HD acyl chain alignment distribution at monolayer coverage for graphitic substrates of varying curvature. The insets show the definition of the angle ϕ for the lipids on graphite and CNTs.

Figure 4: At left, the average gauche defect probabilities of the lipid alkyl chains as a function of substrate curvature. Standard deviation is used as the error estimate. At right, the corresponding gauche defect probabilities as a function of tail carbon index, see Figure 1. Dihedral angles between $70 \pm 30^\circ$ were counted as trans-bonds, i.e., gauche defects.

formed CG simulations under conditions that enable saturation of the adsorption. Figure 5 presents the time evolution of the number of adsorbed lipids. Analogous to the atomistic simulations, LPC and DPPC self-assemble first rapidly into micelles and bicelles in the aqueous phase resulting in stepwise increase in adsorption as these micelles and bicelles adsorb on the CNT. In $4\mu\text{s}$, the adsorption amount saturates and no further evolution of the adsorbed morphologies is observed. Figure 6 shows the final adsorption configurations as simulation snapshots. The DPPC lipids rise to a perpendicular orientation with respect to the surface and the LPC lipids form helical micellar striations on the CNT. Notably, the tubular DPPC coating on the (18,0) CNT remains incomplete by visual analysis (part of the CNT surface is uncoated) indicating more lipids are likely to adsorb given more time. Thermal equilibrium in the sense of equilibrium between desorption and adsorption is not reached within achievable simulation time. This is consistent with the high cohesive energy for DPPC-CNT binding (330 kJ/mol)²¹ which indicates that DPPC molecules are unlikely to desorb from CNT surface. However, no further evolution of the helical micellar striations (LPC) and the tubular (DPPC) packing morphologies was observed and the morphologies also already match experimentally¹⁸ and theoretically^{29,30,32} reported ones. Hence, we are confident the observed packing morphologies, that is tubular packing for DPPC vs. helical packing for LPC, correspond to the adsorption morphology in an equilibrated system.

In these packings, the graphite symmetry directions, the CNT axis orientation, and lipid tail bending have less importance than with the monolayer coverages. As it is energetically favorable to shield both the CNT and the lipid tails from water, the lipids typically pack into morphologies that engulf the whole CNT inside the hydrophobic core. Here, the spontaneous curvature (shape) of the adsorbed lipid molecules becomes the dominating factor in determining the resulting packing morphology. In shielding both the lipid tails and the CNT from water, the lipid packing needs to follow the substrate curvature, yet the lipids want to also preserve the shape of their equilibrium aggregate. The equilibrium coating is a result of these two competing interactions.

We next discuss the equilibrium aggregates in terms of a phenomenological argument of total (mean) curvature J to illustrate the adsorbed morphologies as the substrate curvature changes. In aqueous solution, in the absence of a substrate DPPC forms planar bilayers with zero curvature. Even though DPPC has been reported⁷¹ to have slight positive spontaneous curvature ($< 0.068 \text{ nm}^{-1}$) in the following treatment we assume it prefers flat geometries as the effective contribution to elastic energy due to its curvature is small. A cylindrical CNT has a total curvature of $J = \frac{1}{R_{\text{CNT}}}$ only in the radial direction. Therefore, on cylindrical CNTs DPPC adopts a cylinder-like monolayer coating as it eliminates curvature along the axial direction. LPC, on the other hand has a cone-like form leading to spherical micelles in aqueous solution. The spherical micelles have constant curvature on two directions, yet the cylinder is only curved radially. Furthermore, the cylinder curvature does not match the LPC innate curvature, and the resulting stress is relieved by twisting the spherical micelle into a helix on the CNT. Interestingly, the submonolayer LPC coverage also reflects the same twist, and templates the helical micelle packing. On the other hand, DPPC lipids rise and set perpendicular to the substrate, loosing the submonolayer coverage morphology entirely. This is because the cylindrical packing DPPC prefers results in a stronger collective lipid tail-tail cohesion.

Further examination of the morphologies in Figure 6 reveals the tilt angle of the LPC spiral becomes more parallel to the CNT axis as the CNT gets thinner. One reason for this is the more axial orientation of the first (mono)layer of lipids, see Figure 2. On the other hand, the spiral LPC coating is a helical hemicylinder which can be approximated with two principal curvature radii, one along the hemicylinder and other being the helix curvature. Let us now assume that the spontaneous curvature of LPC, $J_{\text{LPC}} = \frac{2}{R_{\text{LPC}}}$, where R_{LPC} relates to the inverse curvature radius (spontaneous curvature) of LPC, enforces a constant mean curvature for the helical aggregate. A trigonometry approximation yields that the helix rise (tilt angle) is $\alpha = \arccos\left(\frac{R}{R_{\text{LPC}}}\right)$, where $2R$ is the diameter of the CNT—lipid aggregate, see Figure 7. As the figure shows, when the CNT gets thinner (diameter decreases), the helix tilt

angle increases to compensate the curvature increase along the CNT circumference. This adaptation allows the helix to maintain constant curvature even though the CNT radius changes. Indeed, Figure 6 shows this clearly with the LPC spiral forming approximately 4 full turns around the (18,0) CNT and 2 around the (10,0) CNT; the periodic boundary conditions and the thinner tube partially fitting inside the micelle core influence the exact number of turns.

Additionally, Figure 6 shows the spiral formation is more complete on the (18,0) CNT than on the (10,0) CNT. This is because the thin CNT fits partially inside the LPC micelle hydrophobic core which deforms the helix form from the hemicylinder. For an even thinner tube, we would expect micellar engulfment. For example, related works on PEGylated lipids^{62,72} and block-copolymers³⁵ show CNTs can be engulfed by polymeric micelles.

Figure 5: Time evolution of the number of adsorbed LPC and DPPC molecules on CNTs of varying diameter in the CG simulations. Lipid coatings have reached full coverage with the exception of the DPPC coating on the (18,0) CNT that has approximately 10 % of the CNT surface uncoated. Despite this, the graphs show that the number of adsorbed DPPC molecules exceeds those of LPC.

Dispersion efficiency

Carbon nanotube bundling in aqueous environment stems from the cumulative effect of both van der Waals attraction between CNTs and the entropic cost of solvating hydrophobic

Figure 6: Snapshots corresponding to final simulation configurations ($4 \mu\text{s}$) of the CG simulations of DPPC and LPC on (18,0) and (10,0) CNTs. LPC forms helical hemimicelles spiraling around the CNT whereas DPPC coats the CNT as a tubular uniform coating. In the visualization, water beads and bulk micelles have been omitted for clarity.

Figure 7: At left, the mean curvature of a helix is visualized by presenting the osculating circle (radius R_{LPC}) of the helix. The helix mean curvature is constant at all points along the contour so the osculating circle forms a uniform circle. At right, illustration of this helix wrapping on two cylinders of radii $R > R'$. By assuming same mean curvature for both helical aggregates, the helix tilt angle α increases with decreasing cylinder radius, $\alpha < \alpha'$ to compensate the curvature increase along the cylinder circumference. The radii of the cylinders correspond to those of the CNT—lipid aggregates.

Table 2: Hydration of the lipid choline groups and the average number of phosphate group - water hydrogen bonds per area and head group (in parenthesis) calculated from the all-atom simulations with submonolayer coverages.

Substrate	Lipid	Choline hydration in H ₂ O molecules /nm ² (/head group)	Phosphate-H ₂ O hydrogen bonds /nm ² (/head group)
graphite	DPPC	7.0 (17.1)	2.29 (5.63)
(36, 0) CNT	DPPC	7.2 (18.3)	2.29 (5.81)
(18, 0) CNT	DPPC	7.4 (18.6)	2.33 (5.88)
(10, 0) CNT	DPPC	7.5 (18.9)	2.36 (5.95)
graphite	LPC	9.3 (16.6)	2.91 (5.20)
(36, 0) CNT	LPC	9.8 (16.8)	3.12 (5.35)
(18, 0) CNT	LPC	10.2 (17.5)	3.13 (5.38)
(10, 0) CNT	LPC	10.9 (18.3)	3.32 (5.58)

Table 3: Number of hydrogen bonds formed by the LPC hydroxyl group (OH) with water, other LPC sites, and in total per area of coated CNT.

substrate	OH-Water nm^{-2}	OH-Other nm^{-2}	Total nm^{-2}
GS	0.631	0.298	0.944
(36, 0)	0.670	0.289	0.967
(18, 0)	0.714	0.279	0.998
(10, 0)	0.753	0.274	1.033

CNT surfaces (hydrophobic effect). For effective dispersion of CNTs in aqueous solution, a surfactant coating needs to, at some finite intertube separation, counter the resulting attraction so that a free energy barrier against reaggregation forms. The attraction scales with the CNT size with large CNTs attracting each other more strongly.

The repulsion is induced by the surfactant head groups: with zwitterionic lipids the important contribution comes from entropy and water interactions of the head group.^{73,74} Unfortunately, the free energy calculations required for estimation of the dispersive efficiency of a surfactant coating are prohibitatively costly for these systems in full atomistic detail. In CG detail, we obtain complete free energy landscape mapping as a function of the CNT separation to get an estimate for the barrier against reaggregation. However, the CG description lacks in degrees of freedom affecting especially the entropic contributions of water behavior, making a free-energy decomposition unreliable. Therefore, we analyze the water behavior around the lipid head groups also in atomistic detail. Finally, the head group density and the head group positioning are related with the hydration data and the resulting dispersion efficiency.

Table 2 shows lipid hydration in the all-atom simulations is largely curvature independent with only a slight increase with curvature. The two lipids have little difference in water bound per head group, and the differences in water bound per area rise from the head group density. As an LPC molecule takes less space than a DPPC molecule, LPC binds 30 – 40 % more water than DPPC in this monolayer morphology. Also the small systematic increase of hydration with curvature can be explained by steric considerations: the head groups rising from the substrate are surrounded by more water if the substrate is curved. This reflects as increased hydration. However, the influence is much smaller than that resulting from the higher density of the LPC head groups. Here, the head group hydration is quantified by calculating the number of water molecules in the first hydration shell of the choline nitrogen (within 5.5 Å of the nitrogen). In calculating the area normalizations, 0.3 nm is added to the radius of the CNT to account for the excluded volume effect, see Ref.³⁷

Besides the number of water molecules involved in the head group hydration, hydrogen bonds with water influence the water binding strength and hydrogen bonds between the surfactants can influence their adsorption morphology. For both DPPC and LPC, the head group phosphate group forms hydrogen bonds with water. LPC has additional hydrogen bonding capacity through its OH group. Table 2 shows the hydrogen bonds corresponding to the phosphate group behave analogous to head group choline hydration: increasing substrate curvature slightly increases the number of hydrogen bonds formed but the major difference comes from LPC having a larger head group packing density. Analogous to difference in hydration, LPC phosphate forms more hydrogen bonds per area covered than DPPC due to the higher packing density. Table 3 shows the hydrogen bonds of the LPC OH group are mostly with water, again with curvature increasing the number of bonds with water. However, the OH groups also bind the adsorbed lipids together by an interconnected hydrogen bond network; the LPC heads form chain-like morphologies in Figure 2 because of the extra OH-hydrogen bonding capability. This reinforces the formation of helices as the helix morphology allows most LPC-LPC inter-lipid OH-phosphate hydrogen bonds. The chain-like lipid binding is more probable for the less curved substrates. This is due to higher curvature increasing water access, and hydrogen bonds with water replacing the ones between lipid head groups. In total, the OH group, and the hydrogen bond provided by it, contributes extra stability to LPC packing morphologies in comparison to DPPC.

In total, the atomistic hydration and hydrogen bond formation results show both lipids bind water similarly, and the essential difference in total water binding and the resulting coating induced repulsion, comes from the head group density in the packing morphology. If the coating induced repulsion is effective at a larger CNT separation, it overlaps less with the van der Waals attraction and a more modest repulsion due to a coating is sufficient for dispersion. Therefore, in addition to the density, also the head group extension from the substrate is a factor in determining the dispersive efficiency. Figure 8 shows the lipid head groups rise off the CNT surface even at a sub-monolayer coverage. The first peak

(at ~ 0.43 nm) corresponds to substrate contact and the second peak (at ~ 0.96 nm) to the heads rising from the substrate to the water. The portion of lipid heads rising to water increases with increasing substrate curvature. As expected, the close to saturated coverages where spiral micelles (LPC) or tubular coating (DPPC) form set the head groups significantly further from the surface. The LPC spirals, see Figure 6, correspond to a much wider distribution between 0.5 nm and 3 nm but the DPPC heads form a more localized peak around 2.3 nm.

Estimating the dispersive effectiveness of the coatings is difficult based on the distributions solely. Therefore, Figure 9 shows the free energy of the two fully coated CNTs crossing at 90° angle as a function of intertube distance calculated with the CG model. The van der Waals attraction between CNTs in water depends on the CNT separation and angle at which the CNTs cross. Assuming the coating is uniform, the 90° angle corresponds to the minimum barrier for reaggregation. The free energy calculation reveals the LPC spiral coating provides a 10 kJ/mol barrier and the DPPC cylindrical coating a 76 kJ/mol barrier. We note the contact repulsion dip in Figure 9 at close-ranges in the free energy potential is an artefact resulting from configurations where a single layer of lipids would fit in-between the CNTs; the lipids freeze upon contact at the employed umbrella sampling time scale.

Why is the DPPC dispersion barrier higher here than the LPC barrier? As noted before, the dispersion barrier of lipid-coated CNTs depends on the hydrophobic attraction between the CNTs, lipid coating density, extension, and hydration. Whereas the CNT hydrophobic attraction is equal for similar CNTs, Figure 10 shows the DPPC coating provides a significantly higher lipid density around the CNT (2.24 DPPC versus 1.61 LPC molecules per nm^2 , calculated from the data of Figure 5) and the lipids extend further from the CNT, see Figure 8. For LPC, the close agreement with the experimental LPC density, 1.51 LPC/ nm^2 for the same CNT¹⁸ indicates saturated LPC coverage. However, more DPPC molecules could adsorb, given more time in the simulations, which would increase the density difference further. Furthermore, the smaller lipid density and extension result in lesser degree of

steric repulsion and higher mobility for LPC molecules on the CNTs further reducing the dispersion efficiency of the LPC coating in comparison to DPPC.

Figure 8: DPPC (left) and LPC (right) head group choline N atom - CNT radial distribution functions at close to monolayer and saturated coverage showing the head group positioning with respect to the CNT surface for atomistic and CG CNTs of varying diameter. The distributions are normalized with the number of adsorbed molecules (molecules within 1.5 nm of the CNT).

Figure 9: The dimerization free energy based on fully coated (18,0) CNT CG simulations as a function of the CNT—CNT center-of-mass distance for two CNTs perpendicular to each other.

Figure 10: The lipid density plots of fully LPC (left) and DPPC-coated (right) (18, 0) CNTs.

Discussion

Here, we investigated the effect of substrate and surfactant curvature on non-ionic surfactant self-assembly at hydrophobic substrate – water interface by molecular simulations. Choosing a model system of two lipids differing in their number of hydrophobic tails but sharing the head group chemistry enables us to assess the influence of surfactant shape on the adsorption morphology. Simulations of the adsorption morphology at different surfactant concentrations and on substrates with varying curvature enable us to isolate the morphology changes to an interplay of competing interactions. Furthermore, we related the findings to dispersion efficiency by free energy calculations, and assessed the relation of the hydration behavior and the adsorbed structure.

We found that both LPC and DPPC form an ordered monolayer on planar graphite and this monolayer orients along the graphite symmetry directions. On curved substrates, LPC forms helical striations at submonolayer coverage. At increasing LPC concentrations,

the morphology changes into helical micellar striations which continuously wrap around the CNT. DPPC, however, prefers in our simulations oriented patches that wrap around the CNTs forming a continuous coverage at submonolayer adsorption. For higher concentrations, the initial monolayer orientation is forfeited and the lipids adopt a tubular micelle form centered around the CNT axis. In total, we found the lipid packing is dictated by the penalty involved in exposing the hydrophobic graphite/CNT substrate or lipid tails to water. For curved substrate such as CNTs, the hydrophobic binding interaction between the lipid tail and the substrate is reduced with increasing curvature. The balance change between hydrophobic binding and curvature-sensing interactions is the main factor inducing morphology changes as the lipids compete with axial and radial packing preferences. For example, the prevalence of the CNT axial orientation and helical vs. ringlike lipid morphologies depend on the magnitude of substrate-tail binding energy compared to tail-tail cohesion and tail bending which are less sensitive to substrate curvature. Head group chemistry, inter-lipid hydrogen bonds, and charge-charge interactions between lipid head groups provide an additional contributing factor which can both stabilize or destabilize a morphology. Furthermore, increasing substrate curvature requires the lipid tails to bend in order to obtain complete coverage (reduce hydrophobic exposure). These tail bending defects compete with the binding of the adsorbed layer resulting in a more dynamic adsorption morphology.

Our observations of an ordered surfactant monolayer on graphite following the graphite axial directions are consistent with calorimetric studies of Refs.^{13,14} where an initial, ordered monolayer is reported. Simulationally the emergence of alignment following graphite symmetry directions due to collective surfactant-surfactant interactions has been reported earlier for ionic surfactants.^{27,75} Upon introduction of substrate curvature, we reported the CNT axial orientation emerges as the preferred orientation on low surface coverages due to the cost of introducing bends. Furthermore, the overall morphologies are consistent with other atomistic simulations done on LPC²⁰ and DPPC.²¹ In Ref.,²⁰ atomistic molecular simulations of LPC-coated CNTs confirmed striations seen in the transmission electron microscope

experiments. However, on multiwalled CNTs, Richard *et al.* have speculated that the various helical striations they observed SDS to produce using transmission electron microscopy would follow the carbon network¹⁶ instead of the CNT axis. Whereas our highest curvature CNTs showed very strong axial preference for the lipids, even partly enforcing them into ringlike morphologies, the axial preference decreases with decreasing CNT curvature. Furthermore, our graphene simulations where substrate curvature vanishes show strong alignment along the symmetry axes. Together these results provide support for the observations of Ref.¹⁶ provided that the diameter of the CNT is sufficiently large.

The spontaneous curvatures of the two lipids correspond to DPPC forming bilayer-like and LPC micellar morphologies in bulk solutions. Furthermore, our LPC observations of helical micellar striations at higher concentrations are consistent with the experimental¹⁹ and the simulational^{29,32} works. However, atomistic simulations by Wang *et al.*²² show at the low concentration range for DPPC both aligned structure and tail wrapping around the CNT. As their simulation duration is ≈ 15 ns, this could be an initial aggregation structure. In addition, a CG study performed by Wallace and Samson³² suggested random adsorption model whereas our atomistic simulations mostly show ordered patches. The more random adsorption in Ref.³² is likely due to the CG procedure smoothening the atomistic details which decreases the effect of tail alignment along the CNT symmetry axes. Furthermore, the simulation results for DPPC are very similar to those reported by Suttipong et al. for adsorption of branched SDBS on CNTs.²⁴ Although SDBS is chemically quite different from DPPC, the studied branched SDBS shares some characteristics with a two-tailed lipid. This similarity in the findings shows the applicability of the results could be broadened.

Most of the LPC helices in our atomistic simulations (corresponding to the initially formed adsorption monolayer) are formed of single lipids side-by-side whereas a number of experimental studies appear to indicate single-tailed surfactants form hemicylindrical aggregates on graphite on top of the initially formed monolayer, see e.g.^{13,14,76} This would correspond to a monolayer formed of columns of lipids opposing each other. The lipids adopting

a side-by-side structure in our simulations is likely a concentration dependent phenomenon (opposing lipid morphology induced only upon further adsorption) and also possibly influenced by the finite size of the simulations box. Similar findings have been reported for SDS monolayers.²⁷

In total, our findings on adsorption morphology changes with curvature above are in full agreement with the MD simulations of Tummala *et al.* on SDS behavior.³⁷ In their work, SDS formed micellar structures on planar substrate but positively curved substrate induced lamellar and negatively curved substrate cylindrical lamellar aggregates.³⁷ Additionally, they reported changes in surfactant concentration and substrate curvature to significantly influence surfactant orientation, head group-head group distribution and head group-counterion packing.³⁷ Also in agreement with our results, Tian *et al.* found that beyond a critical curvature value, surface geometry governs the self-assembly of amphiphilic molecules and the shape of the aggregates.³⁹ Their theoretical model indicated that the morphological transitions from bilayer to cylindrical structures on highly curved surfaces are mainly induced by the sharp increase of bending energy of bilayer morphologies with surface curvature.³⁹ In comparison to the more simple surfactants such as SDS studied in prior works,^{26,37,77} we find the zwitterionic LPC head groups form connected, hydrogen bonded networks. The inter-lipid hydrogen bonds both stabilize and reinforce the helical packing as it enables a relatively large number of hydrogen-bond bridges between phosphate-hydroxyl groups of neighboring lipids. The stabilizing effect is also present in lipid membranes that have inter-molecular hydrogen-bonding networks. There they decrease the areas per lipid and increase the melting-temperatures.⁷⁸ The coating aggregate dynamics is an important factor both for dispersion and adsorbed morphology: in our simulations, high local curvature causes the lipids to remain in liquid-disordered, fluidic state. However, at the same temperature on a substrate with smaller curvatures and planar graphite substrate, the lipids freeze in liquid-ordered phase due to larger substrate contact area. Interestingly, calorimetric studies by Király and Findenegg suggest that surfactant half-cylinders on planar graphite are tem-

plated by an ordered monolayer in which adsorption is nearly irreversible.^{13,14} The degree of freezing we observe for the adsorbed monolayer, with the exception of extremely small CNTs, corresponds to such, very tight substrate binding. Similar substrate induced nucleation and freezing upon adsorption in comparison to bulk aqueous aggregates has been reported for anionic SDS.²⁷

Additionally, we examined the aqueous dispersion efficiency of the lipid coatings directly by free energy calculations, and indirectly by assessing the relation between head-group hydration and the morphology geometry. While charged lipids repel each other by electrostatic double-layer forces, phosphatidylcholine lipids are zwitterionic and have very small electrostatic repulsion. Instead, the repulsive barrier arises from entropic changes in water due to hydration of the head groups.⁷³ While the cohesive van der Waals energy between two CNTs is large at very short distances, it decays fast (r^{-6}). Therefore the distance at which the hydration repulsion occurs⁷⁹ (the radial extension of the PC head group) plays important role in CNT solubility. On the other hand, the CNT van der Waals attraction is heavily CNT diameter dependent making small CNTs easier to solubilize as shown experimentally.^{11,12}

First, we examined the submonolayer coverages, and reported that both head group hydration and lipid—water hydrogen bond number increase slightly with substrate curvature. We note classical water models differ in their hydration prediction, see e.g. Ref.,⁸⁰ and the specific values obtained here could be subject to change, if a different water model was used in the simulations. However, since both lipids have the same headgroup, the dominant determining factor is lipid density in the adsorption morphology. At submonolayer coverage, LPC provides superior density due to a DPPC molecule covering more substrate area than LPC. However, at higher concentrations the head group densities reverse; at close to saturated coverages the DPPC tubular coating results in higher lipid density than the helical micellar coating formed by LPC. The DPPC head groups also extend further than those of LPC. Yet, a higher DPPC v/w concentration is needed to fully saturate the DPPC morphology than LPC. As a consequence, we expect LPC to provide initially a higher

repulsion than DPPC but the complete tubular packing of DPPC will ultimately result in a higher dispersion barrier than that induced by LPC helical striations. Indeed, our CG free energy calculations of fully coated CNTs resulted in dispersion barriers of 76 kJ/mol and 10 kJ/mol for DPPC and LPC respectively.

LeNeveu *et al.* have calculated the repulsion for phosphatidylcholine based on osmotic stress experiments^{79,81} and reported that the energy needed to bring two DPPC bilayers to 0.15 nm separation is 50 kJ/mol/nm².⁷⁹ Our free-energy calculations with fully coated crossed CNTs result in a point-like contact. Due to the different geometry, a direct comparison with the results of LeNeveu *et al.* is not feasible. However, one could perhaps qualitatively assume that upon contact the tube-tube interaction lies on a 1 nm² patch which would make the observed barrier values somewhat in line with those of LeNeveu *et al.* Furthermore, LeNeveu *et al.* also showed that at short interbilayer distances, the attractive van der Waals forces in the system are negligible compared to repulsion by hydration.⁸¹ Extending the comparison to dispersion efficiency by lipids is challenging as experimental data on pure DPPC-CNT systems is scarce, as most studies deal with various lung-like dispersant mixtures. Solubility data for dimyristoylphosphocholine (DMPC) differing only in hydrocarbon tail length from DPPC, however, seems to indicate that double-tailed lipids are poor dispersing agents for CNTs in comparison to LPC¹⁸ contradicting our findings.

The reason could lie in CMC of DPPC being in the nm range.⁶⁶ At concentrations above CMC, DPPC readily forms vesicles and the vesicle formation competes with direct adsorption of lipids on the CNT. At concentrations corresponding to the dispersion studies, see e.g.,^{18,82} almost all the lipids can be expected to form aggregates in the solution, and the amount of free DPPC lipids is very low (approximately CMC). A CNT introduced into this solution can obtain a lipid coating either by lipid aggregates from the solution adsorbing on the CNT or by adsorption of individual lipids. Specifically, a recent study by Sato and Sano⁸² reports adsorbed molecules, and not encapsulation by vesicles, are responsible for dispersion in a system of double-tailed lipids and CNTs. In our simulations, individual lipids, while

available, readily adsorbed to the CNT but the system runs out of free lipids as they form aggregates in the solution. These aggregates adsorb in the simulations while significant regions of CNT remain uncovered. In our simulations, we observed aggregate adsorption to slow down and come to a halt (at simulation time scale) when the exposed CNT region was smaller than the characteristic aggregate size in the solution. Hence, we speculate lipid adsorption from the vesicular aggregates might become kinetically trapped, and as the free DPPC concentration is extremely low, the CNTs may not obtain a perfectly saturated cylindrical coating before re-aggregating. This speculation is supported by the adsorption isotherms of Ref.⁸² which show that shorter chain phosphatidylcholines which have higher CMC, and thus more free lipids in the solution, show an increase in the dispersed amount. Douroumis et al. reported similar results.⁴⁰

On the other hand, with LPC, the amount of free lipids in the solution is significantly higher (LPC CMC is in the μM range⁶⁶) but more importantly, LPC micelles are smaller than DPPC vesicles which facilitates their adsorption on the CNT surface. Due to the high spontaneous curvature of LPC, LPC micelles have small aggregation numbers of approximately 100-200 molecules.⁸³ Aggregates of this size readily adsorb which means the surface coverage is likely to rapidly saturate. This speculation is supported by the observed LPC adsorption behavior in our simulations and the excellent agreement between our simulation and experiments (LPC surface coverage of 1.61 LPC/nm² in the simulations and 1.51 LPC/nm² in Ref.¹⁸). Based on these considerations, we think measurements or calculations of adsorption isotherms relating the amount of adsorbed molecules and concentration would be necessary for full understanding of CNT dispersion. Ref.⁸² presents experimental adsorption isotherms for double tailed lipids and Ref.⁸⁴ calculated ones for a related system. Understanding the adsorption isotherms in terms of dispersion control requires knowledge of the equilibrium adsorption morphologies both on the substrate and in bulk aqueous solution. For these, understanding the role of both molecular and substrate curvature is important as it can provide direct information about the expected morphologies and their behavior.

Conclusions

In conclusion, we find lipids efficiently cover and disperse nanoscale hydrophobic objects of a variety of local curvatures in water solutions. The dispersion efficiency effectively depends on the head-group density and their extension from the hydrophobic substrate making the adsorption morphology highly important in controlling dispersion. In summary of the submonolayer coverage examinations, we find the adsorption morphology at submonolayer coverages on curved graphitic substrates is dictated by four competing interactions. These are preferences to 1) maximize lipid tail - substrate interaction area and lipid tail - lipid tail interaction area, 2) orient the hydrocarbon tails along the graphite lattice principal axes, yet 3) minimize hydrocarbon tail bends (gauche defects), and 4) optimize the lipid head group packing interactions. In total, the packing morphologies arise from these interactions with the molecular specifics of the adsorbed species and substrate curvature dictating the balance. For higher lipid coverages, where lipid self-adhesion and collective effects become dominant, we find the lipid shape and geometrical considerations dictate the packing - the packing morphologies can be understood in terms of curvature arguments, and shielding the lipid tails and the hydrophobic substrate from water with the aforementioned four contributions as co-contributors.

The work shows curvature of both the substrate and the adsorbing amphiphilic molecule is an important factor in determining adsorption morphologies on hydrophobic substrates in aqueous environment. Furthermore, we reported how the resulting coating morphology relates with resulting aqueous dispersion efficiency, and discussed the control factors. In terms of engineering dispersive and protective coatings, the findings could provide directions toward designing coatings with general size or object form dependent function especially in terms of aqueous solubility.

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