

CHAPTER III

EXPERIMENTAL

3.1 Equipment and Materials

3.1.1 Equipment

Desktop computer (Intel® Core™ i7, CPU 860, 2.80 GHz, RAM 4 GB, Window 7, and Microsoft Office 2007)

3.1.2 Software

3.1.2.1 *LAMMPS molecular dynamics simulation package*

3.1.2.2 *Visual Molecular Dynamics (VMD), version 1.9*

3.1.2.3 *Microsoft Visual Studio 2005*

3.1.2.4 *WinSCP*

3.1.2.5 *PuTTY*

3.2 Simulation Method

The detailed derivation of DPD method is available in the work of Groot and Warren (Groot and Warren 1997) and Groot and Rabone (Groot and Rabone 2001). The simulated system in this work consists of water, SDS surfactant, and carbonaceous nano-particles (GS, GOS, GN and GON). The degree of coarse graining (N_m), or the bead density, was chosen to be 5 water molecules per bead ($N_m = 5$). With the volume of one water molecule approximately equal to 30 \AA^3 (Lu et al., 1993), the volume of one DPD bead in our system is $\sim 150 \text{ \AA}^3$.

The approximate total volume of one SDS molecule is 410 \AA^3 (Tanford 1972; Takahash.Y et al., 1973; Nagarajan and Wang 2000), approximately equivalent to the volume of 3 DPD beads. In our formalism, two consecutive beads mimic the “tail” of SDS, and the third bead mimics the “head”. A schematic of the coarse-graining scheme is shown in Fig. 3.1

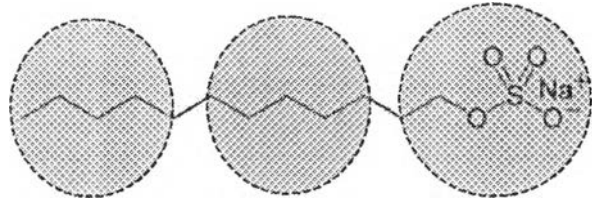


Figure 3.1 Partitioning SDS molecule into DPD beads.

The morphology of one SDS molecule was preserved by applying harmonic spring bonds of equilibrium length $1.0126 R_C$ between two consecutive beads, with spring constant $100 \frac{k_B T}{R_C}$ (Rekvig et al., 2003), k_B is Boltzmann's constant, T is temperature and R_C is the dimensionless unit length of the system. The arbitrary density of this simulation is set to $5 \frac{\text{beads}}{R_C^3}$, where R_C is a dimensionless unit length of our simulation. By plugging in the value of a bead volume, $R_C = \sqrt[3]{5 \times 150} = 0.90856$ nm.

For the carbonaceous nanoparticles, one hexagonal ring of carbon atoms has the approximate volume of 148 \AA^3 (Min et al., 2012). As shown in Fig. 2, the carbon atoms in graphene were grouped in beads and were arranged in the necessary angles. The whole carbon nano-sheet is treated as a single rigid body to maintain the bond lengths and angles

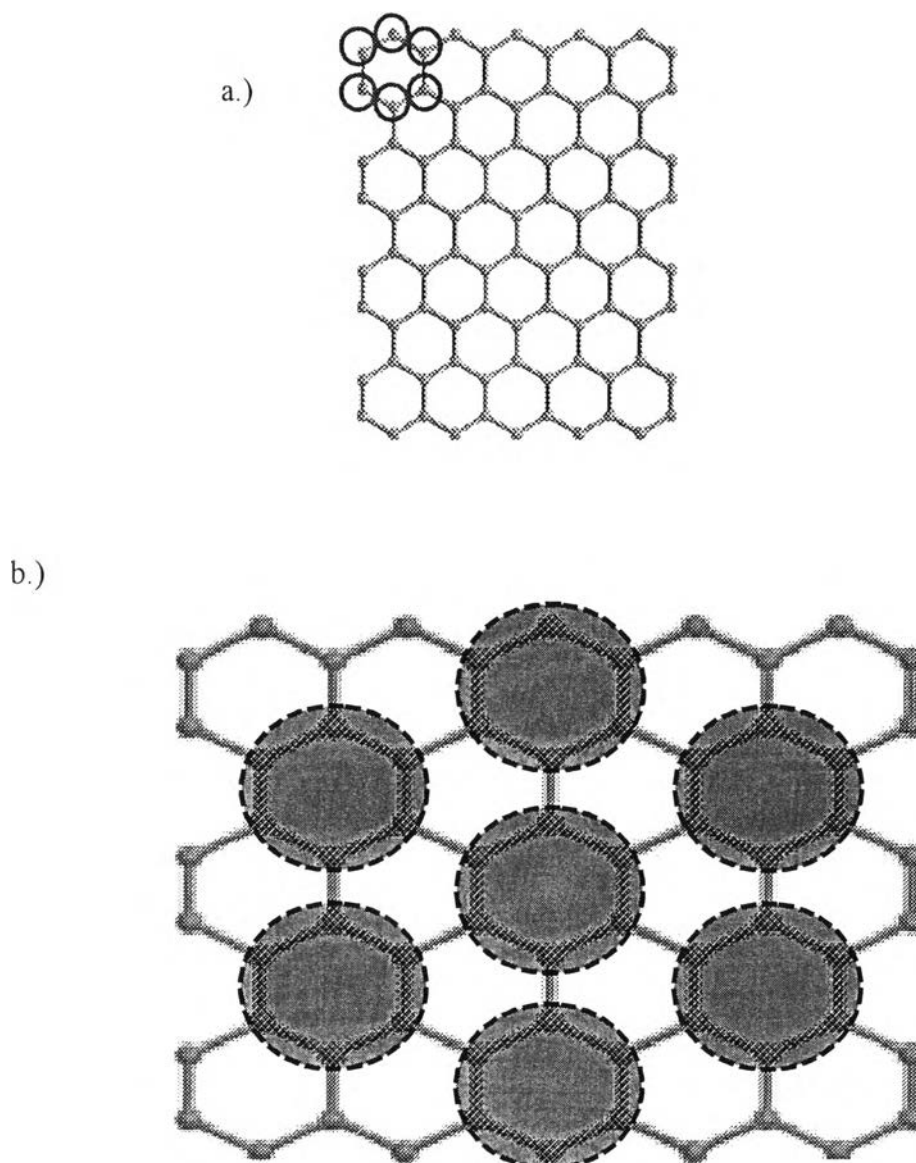


Figure 3.2 a.) Schematic representation of carbon atoms on graphene sheet. The small spheres in the red circles are carbon atoms. They are connected with bonds to form hexagonal rings. b.) Schematic representation of partitioning graphene hexagonal rings into DPD beads (black circles).

Both GS and GN were simulated as soft-core rigid colloid particles, as proposed by Koelman and Hoogerbrugge (Koelman and Hoogerbrugge 1993). GSs were represented as squares, and GNs were represented as infinitely long rectangles.

Time scale of our DPD simulation is expressed as a function of τ . It is a dimensionless time, which can be calculated with the equation $\tau = \frac{N_m D_{sim} R_C^2}{D_{water}}$. D_{sim} in our simulations was obtained by simulating pure water for 65000 time steps. Then, the value of mean-square displacement of water beads, or $R_{W_r}^2$, was calculated. The gradient of the plot $\frac{R_{W_r}^2}{\epsilon}$ against τ is equal to D_{sim} (Groot and Rabone 2001). In our case $D_{sim} = 0.0025 \frac{(R_C^2)}{\tau}$. Because the self-diffusion of water is $D_{water} = (2.43 \pm 0.01) \times 10^{-5} \frac{cm^2}{s}$ (Partington et al., 1952), we obtain $\tau = 4.25$ ps for our simulations.

The dimensions of the GSs were fixed to 3x3, 6x6 and 12x12 nm², and the widths of the GNs were fixed to 3 nm, 6 nm and 12 nm. In Table 3.1, we report the dimension of each GS and GN considered here.

Table 3.1 Dimensions of GSs and GNs in this simulation

Type	Dimension in X-axis (nm)	Dimension in Y-axis (nm)
GS	3	3
	6	6
	12	12
GN	3	Infinity
	6	Infinity
	12	Infinity

We simulated GOS and GON by making the beads on the edges of GS and GN hydrophilic. In Fig. 3.3, we show the representative of GS, GOS, GN and GON in this simulation

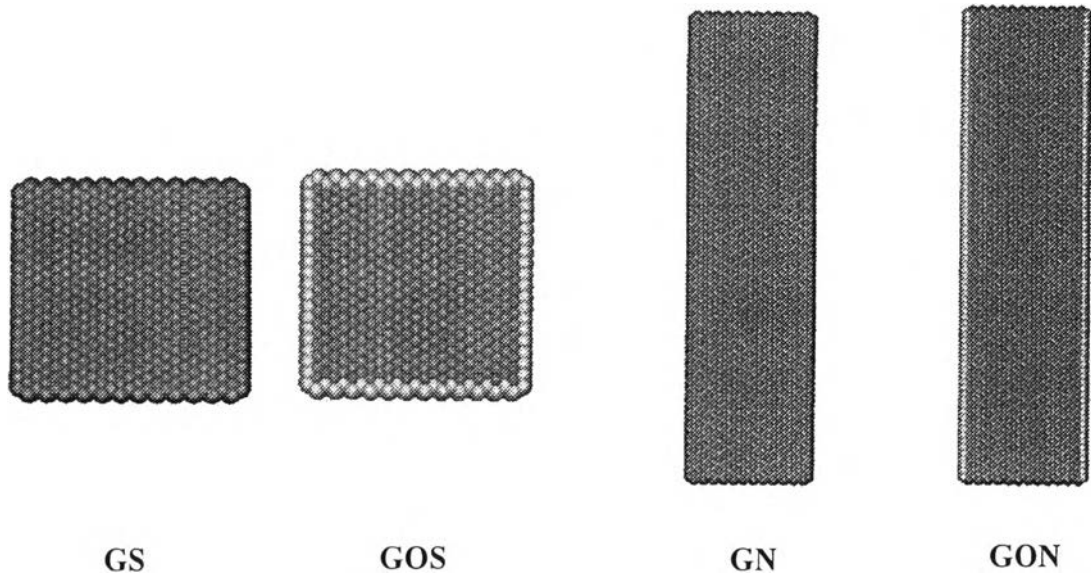


Figure 3.3 Schematic representations of $6 \times 6 \text{ nm}^2$ GS, $6 \times 6 \text{ nm}^2$ GOS, 6-nm-wide GN and 6-nm-wide GON. The yellow beads represent the pseudo-oxide edges, treated as hydrophilic beads.

In our simulations, five types of beads are present; water (w), SDS hydrophilic head (h), SDS hydrophobic tail (t), carbon (c), and pseudo-oxide edge (e). These beads interact with each other as described by intra-species (a_{ii}) and inter-species repulsion parameters (a_{ij}). Parameters a_{ii} and a_{ij} are related by $a_{ij} = a_{ii} + 1.447\chi$; $a_{ii} = \frac{75k_B T}{\rho}$ (Groot and Warren 1997), where χ is Flory-Huggins parameter. Because $\rho = 5$ in our simulation, and $k_B T = 1$ (Groot and Warren 1997), a_{ii} equals 15 for every pair of beads of same type. The parameter is changed depending on the beads described. The repulsion parameters used in our simulation are the same as the parameters used by Kuo and coworkers. (Kuo et al., 2004). The parameters are shown in Table 3.2

Table 3.2 Repulsion parameters, a_{ij} , of water, (w), SDS hydrophilic head, (h), SDS hydrophobic tail, (t), carbon, (c), and pseudo-oxide edge, (e). The parameters are dimensionless

	w	h	t	c	e
w	15	0	81	81	0
h	0	15	69	69	15
t	81	69	15	15	69
c	81	69	15	15	15
e	0	15	69	15	15

Following Groot and Warren (Groot and Warren 1997), the change of positions and interactions of all beads follow the Newton's equation of motion $m \frac{dv_i}{dt} = \sum_{j \neq i} F_{ij}^C + \sum_{j \neq i} F_{ij}^S + \sum_{j \neq i} F_{ij}^D + \sum_{j \neq i} F_{ij}^R$; where m is the mass, v is the velocity, t is time, F_{ij}^C is conservative force, F_{ij}^S is harmonic spring force, F_{ij}^D is a random force, F_{ij}^D is a dissipative force and F_{ij}^R is a random force. The dissipative force and random force are defined as $F_{ij}^D = -\gamma w^D(r_{ij})(\hat{r}_{ij} \cdot v_{ij})\hat{r}_{ij}$ and $F_{ij}^R = -\sigma w^R(r_{ij})\theta_{ij}\hat{r}_{ij}$ respectively. The γ is the noise parameter and σ is the amplitude. They are related with the correlation $\sigma^2 = 2\gamma k_B T$. With value of $\sigma = 3$ and value of $k_B T = 1$ (Groot and Warren 1997), the noise parameter (γ) was set to 4.5. The equations of motion were integrated, using the velocity-Verlet algorithm (Groot and Warren 1997). The time step (Δt) was 0.03 τ . LAMMPS was used to carry out the DPD simulations (Deng et al., 2012). The dimension of every simulations box is $27.72 \times 27.72 \times 27.72 R_C^3$, with periodic boundary conditions applied along X, Y and Z dimensions.

To determine the amount of surfactant adsorbed on one nano-particle, as a function of bulk surfactant concentration, one carbonaceous nano-particle was fixed in the middle of the simulation box. The infinitely long axis of GN and GON lied along the Y-axis of the simulation box, and every nano-particle was parallel to XY-plane. The initial configuration was created by placing the desired amount of SDS on both sides of the carbonaceous nano-particles, with their tails perpendicular to the nano-particles. The amount of water beads was adjusted to maintain the density of $5 \frac{\text{beads}}{R_C^3}$. We chose the surface coverage of $0.5 \text{ nm}^2/\text{SDS molecule}$ for our simulations, because when we tried to achieve other coverage which were below $0.5 \text{ nm}^2/\text{SDS molecule}$, the surfactants in the simulation boxes increased. This increased the probability of surfactant micellisation. Once the micelles were formed, they did not adsorb on the surface, so the nominal surface coverage was not achieved. Another problem was the pseudo-oxide edges that prevented some surfactants from adsorbing on them, due to their hydrophilicity. The population analysis results for the SDS on nano-particles are shown in Table 3.3

Table 3.3 Population analysis results for SDS molecules on different nano-particles, at different coverage

Type of nano-particle	Dimension	Number of SDS simulated	Nominal surface coverage ($\text{nm}^2/\text{SDS molecule}$)	Average number of adsorbed SDS	Average number of non-adsorbed SDS	Effective surface coverage ($\text{nm}^2/\text{SDS molecule}$)
GS	$3 \times 3 \text{ nm}^2$	60	0.3	60	0	0.3
	$6 \times 6 \text{ nm}^2$	240	0.3	240	0	0.3
	$12 \times 12 \text{ nm}^2$	960	0.3	715	245	0.402797

Table 3.3 Population analysis results for SDS molecules on different nano-particles, at different coverage (cont.)

Type of nano-particle	Dimension	Number of SDS simulated	Nominal surface coverage (nm ² /SDS molecule)	Average number of adsorbed SDS	Average number of non-adsorbed SDS	Effective surface coverage (nm ² /SDS molecule)
GOS	3×3 nm ²	60	0.3	32	28	0.5625
	6×6 nm ²	240	0.3	184	56	0.391304
	12×12 nm ²	960	0.3	711	249	0.405063
GN	3-nm wide	554	0.3	542	12	0.306863
	6-nm wide	1108	0.3	818	290	0.40665
	12-nm wide	2216	0.3	1634	582	0.407148
GON	3-nm wide	554	0.3	554	0	0.3
	6-nm wide	1108	0.3	808	300	0.411683
	12-nm wide	2216	0.3	1500	716	0.44352
GS	3×3 nm ²	45	0.4	45	0	0.4
	6×6 nm ²	180	0.4	180	0	0.4
	12×12 nm ²	720	0.4	573	147	0.502618

Table 3.3 Population analysis results for SDS molecules on different nano-particles, at different coverage (cont.)

Type of nano-particle	Dimension	Number of SDS simulated	Nominal surface coverage (nm ² /SDS molecule)	Average number of adsorbed SDS	Average number of non-adsorbed SDS	Effective surface coverage (nm ² /SDS molecule)
GOS	3×3 nm ²	45	0.4	34	11	0.529412
	6×6 nm ²	180	0.4	180	0	0.4
	12×12 nm ²	720	0.4	586	134	0.491468
GN	3-nm wide	416	0.4	416	0	0.4
	6-nm wide	832	0.4	672	160	0.495
	12-nm wide	1664	0.4	1332	332	0.499459
GON	3-nm wide	416	0.4	416	0	0.4
	6-nm wide	832	0.4	684	148	0.486316
	12-nm wide	1664	0.4	1327	337	0.501341
GS	3×3 nm ²	36	0.5	36	0	0.5
	6×6 nm ²	144	0.5	144	0	0.5
	12×12 nm ²	576	0.5	576	0	0.5

Table 3.3 Population analysis results for SDS molecules on different nano-particles, at different coverage (cont.)

Type of nano-particle	Dimension	Number of SDS simulated	Nominal surface coverage (nm ² /SDS molecule)	Average number of adsorbed SDS	Average number of non-adsorbed SDS	Effective surface coverage (nm ² /SDS molecule)
GOS	3×3 nm ²	36	0.5	36	0	0.5
	6×6 nm ²	144	0.5	144	0	0.5
	12×12 nm ²	576	0.5	576	0	0.5
GN	3-nm wide	333	0.5	333	0	0.5
	6-nm wide	666	0.5	666	0	0.5
	12-nm wide	1331	0.5	1331	0	0.5
GON	3-nm wide	333	0.5	333	0	0.5
	6-nm wide	666	0.5	666	0	0.5
	12-nm wide	1331	0.5	1331	0	0.5

The simulation was conducted in the NVT canonical ensemble, in which the number of beads, simulation box volume and temperature were kept constant (106480 beads, $27.72 \times 27.72 \times 27.72 R_C^3$ and $1 k_B T$, respectively). There was an exception for the SDS-water systems, which were conducted to calculate critical micelle concentration and micelle radius. The number of beads and simulation box volume of these systems were 92610 beads and $21 \times 21 \times 42 R_C^3$. Simulation time of every system

was set to 1.1475 μs . The trajectories of the last 127.5 ns of every simulation were output every 0.1275 ns, and were used for data analysis.