Functionalization Pattern of Graphene Oxide Sheets Controls Entry or Produces Lipid Turmoil in Phospholipid Membranes

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DPD: The computational approach

The Dissipative Particle Dynamics, DPD, employed here is a thermostat.[1] It complies with Newton's laws and satisfies fluid dynamics. The cost to pay is two-fold. The first compromise is that a Brownian component is explicitly included in the description of the motion, as is the case in Langevin's dynamics. The second concession to practicality is the necessity to introduce a relationship between Brownian and dissipation components of the nanoparticle motion. Under these conditions the time step used in the integration of the equation of motions can be made (much) longer than that used in standard molecular dynamics. Long time-steps, however, can be of little or no use if the weight of a particle is small. Light particles, such as atoms, vibrate at a high frequency. A long time step may encompass several oscillations and therefore introduce great instability in the algorithm that integrates the equations of motion, regardless of the fact that the thermostat would allow its use. The use of the DPD thermostat becomes efficient with particles heavier than atoms, which entail low frequency motions. Coarse graining can effectively produce lower frequencies. The coarse graining of the atomistic structure can be achieved in many different ways. The choice here, as in many DPD applications, is to use soft sphere potentials.[2] These potentials can be traced back to Hildebrand's theory of real solutions or to Flory-Huggins' theory of polymers.[3] They describe hydrophilic and hydrophobic interactions, which are at the core of the interaction between graphenes and phospholipid bilayer membranes.

Validation of the DPD parameters used in the simulations.

Experimentally, Vasudevan and Lakshmi[4] sealed 0.05 g of graphene in 75 ml of solutions of phosphate. After agitation, at pH=7 and 303 K, they were able to obtain the data reported in table S1.

Table S1. Phosphate adsorption on graphene.

Initial phosphate concentration (g/l)	Adsorbed(g/l)[a]	Adsorbed mass (g)	Reciprocal adsorbed mass (g-1)	Final concentration in solution (g/l)	Reciprocal final concentration (l/g)
0.025	0.02111	0.00158325	631.6	0.00389	257.07
0.050	0.04678	0.0035085	285.0	0.00322	310.56
0.075	0.06867	0.00515025	194.2	0.00633	157.98
0.100	0.08937	0.00670275	149.2	0.01063	94.07
0.125	0.1163	0.0087225	114.6	0.0087	114.94

The equation that links the reciprocal of the final concentration in solution (1/x) vs the reciprocal of the adsorbed mass (1/N) linearizes the Langmuir isotherm and reads

$$\frac{1}{N} = \frac{1}{AKx} + \frac{1}{A} \tag{1}$$

where A is the mass at perfect coverage and K is the adsorption constant. The fit with the data of Table 1 can be done for the three central values with a correlation coefficient r = 0.999, A^{-1} = 92.93 g^{-1}; $(AK)^{-1}$ = 0.621. The total mass adsorbed at perfect coverage is therefore 0.0108 g; the Langmuir constant is 149.1 l/g. The perfect coverage implies that in 0.05 g of graphene there are $N_A*0.0108/94 = 6.8*10^{19}$ molecules, where N_A is the Avogadro number. In practice, there is a phosphate ion every 36.6 carbon atoms (or every 9 fused hexagonal rings), which is equivalent to a surface area of 47.2 $Å^2$. The value of the surface area available for each phosphate is calculated regardless of the face where adsorption takes place.
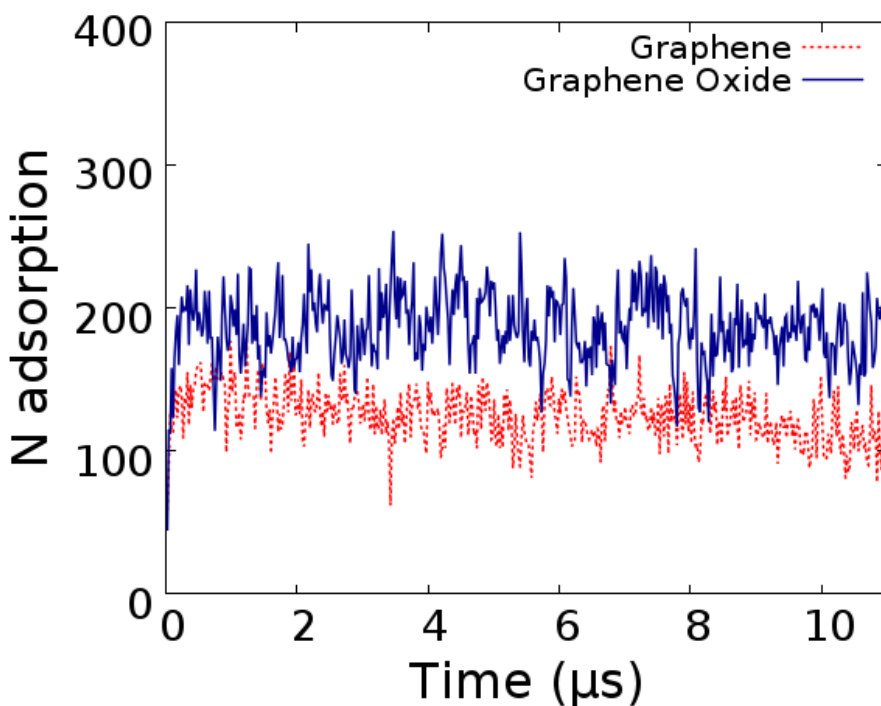
Figure S1. Number of phosphates, N, adsorbed on GS and GOS in the simulations.

Figure S1 compares the number N of phosphates (H-beads) that are adsorbed on graphene (GS) and graphene oxide (GOS) during the simulations where there are 92747 beads of water, 5124 beads of phosphates and 433 beads of graphene or graphene oxide. A dynamical equilibrium is reached with only a small fraction of the phosphates adsorbed (2.4% for GS, 3.6% for GOS, in the conditions of the simulation), which implies that maximum coverage is reached in the calculations.

The surface area of the flake in the simulation is 4261 Å^2. The number of phosphates adsorbed on a GS should be ~90/180 considering one/two faces of the graphene sheet as available for the adsorption. In the simulations, for graphene, the number of phosphates adsorbed is 124.4±18.0 The agreement between the experimental and the calculated number of phosphates adsorbed on GS validates the parameterization used here. For GOS the number of phosphates adsorbed is 186.5±23.8, with GOS that is able to adsorb more phosphate ions.
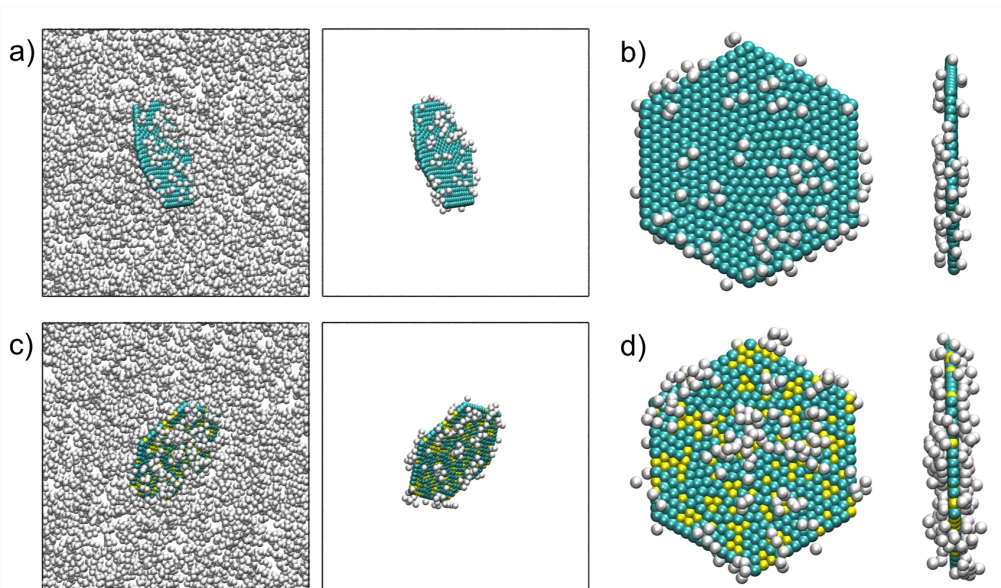
Figure 2. a) H-groups in the simulation box and adsorbed on GS; b) H-groups adsorbed on GS; a) H-groups in the simulation box and adsorbed on GOS, b) H-groups adsorbed on GOS; in the last snapshot of the simulations.

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