**Understanding the Stabilization of Liquid-Phase-Exfoliated Graphene in Polar Solvents: Molecular Dynamics Simulations and Kinetic Theory of Colloid Aggregation**

**Objective**

In the present work, we studied the interactions of graphene with five polar  
solvents [water, DMF, NMP, dimethyl sulfoxide (DMSO), and *γ*-butyrolactone (GBL)] using large-scale MD simulations. The potential of mean force (PMF) between two parallel graphene sheets in each of these solvents was simulated in order to investigate the thermodynamic stability of the graphene dispersion in that solvent.

**Methodology**

In the work presented here, we carried out MD simulations with the *NPT* ensemble (constant number of atoms *N*, constant pressure *P)* 1.0 bar, and constant temperature *T)* 298.15 K) using the GROMACS 4.028 software package and the *o*ptimized *p*otentials for *l*iquid *s*imulations *a*ll *a*toms (OPLS-AA) force field. All of the carbon atoms in graphene were treated as uncharged Lennard Jones (LJ) spheres. The water molecules were simulated using the standard SPC/E model. The bond lengths for water molecules during the simulations were constrained using the SETTLE algorithm. Bond lengths in the solvent molecules were constrained using the parallel version of the LINCS algorithm. The vdW interactions were treated with a cutoff distance of 0.9 nm. The vdW attractions and steric repulsions between different atoms were calculated from  
the LJ potential using the standard geometric averaging rule as implemented in the OPLS-AA force field. Long-range electrostatic interactions were treated using the particle-mesh Ewald (PME) summation method. The equations of motion were integrated with a time step of 2  
fs using the Verlet (leapfrog) algorithm. The velocity-rescaled Berendsen thermostat was implemented to maintain the system at a constant temperature. The pressure was coupled to an isotropic Berendsen barostat. Periodic boundary conditions were applied in all three directions. The trajectories, velocities, and forces corresponding to all the atoms in the system were saved every 10 000 steps (20 ps) to satisfy the ergodicity criterion for data analysis. To investigate the interactions between two parallel graphene sheets in each solvent, we calculated the PMF by numerically integrating (with the trapezoidal method) the interaction forces required to separate the two parallel and fixed graphene sheets at various intersheet separations. This integration process started at the largest intersheet separation (15 Å), at which the PMF was set to be zero, and ended at the smallest intersheet separation simulated (3.2 Å). Since the interaction between two parallel graphene sheets requires 1-3 ns to reach equilibrium, each simulated system was equilibrated for 10 ns. For the systems simulated at various intersheet separations, only the last 5 ns of each simulation was used for data analysis, including the PMF calculations

**Findings**

According to the simulated PMF as a function of intersheet separation, this is due to fact that the enormous vdW interactions that operate between the graphene sheets are responsible for  
the lowest energy minimum in the PMF. Dominant energy barrier results from the interactions of a single layer of confined solvent molecules with the two parallel graphene sheets. The increase in the steric repulsions between the solvent molecules and graphene is the origin of the energy barrier responsible for repelling the graphene sheets. Therefore, when the interactions between graphene and the confined solvent molecules are stronger, the solvent molecules prefer to be confined in a narrower intersheet space, resulting in a higher energy barrier that hinders recombination of the graphene sheets.

**Keywords**

Steric Repulsions

Steric repulsion refers to the arrangement of atoms in a molecule. These effects arise from the fact that each atom within a molecule occupies a certain amount of space.