Solvent interactions with two-dimensional materials: A computational investigation of the dispersion of graphene monolayers in commonly used solvents

Urvesh Patil
Nuala Caffrey
School of Physics and CRANN, Trinity College Dublin, Ireland
upatil@tcd.ie

Maintaining stable dispersions of two-dimensional (2D) materials is a prerequisite for several applications, including surface coatings, printed circuits and some electronic devices. The dispersions are typically produced by the liquid phase exfoliation (LPE) of layered materials. The stability of the solution, i.e., the ability of a solvent to maintain an adequate concentration of suspended flakes over time, is strongly dependent on the chosen solvent [1]. To identify an optimal solvent for a particular 2D material, it is important to determine the role of (i) the initial exfoliation (ii) the free energy of solvation and (iii) the reaggregation rate, the latter two of which will depend strongly on the nature of the solvent – solute interface.

Here, we use density functional theory (DFT) and molecular dynamics (MD) to investigate the stabilization mechanism. We show that solvent molecules interact via a van der Waals (vdW) interaction with the monolayers, with negligible charge transferred between the two [2]. We find that distinct solvation shells are formed around the 2D layer (Figure 1). The first solvation shell is formed irrespective of the nature of solvent (i.e., whether polar or non polar) due to vdW interactions. This first shell then interacts with rest of the solvent via a combination of both electrostatic and dispersion forces. We show that the formation of these solvation shells is always favourable by calculating the enthalpic and entropic contributions to the free energy of interaction. However, energetic considerations such as these cannot explain the experimental solvent-dependence. Instead, kinetic effects can dominate. We find that interfacial solvent molecules with high diffusion coefficients parallel to the graphene layer result in the lowest experimental concentration of graphene in solution. This can be explained by the enhanced ease of reaggregation in the high diffusion regime (Figure 2). Solvents with smaller diffusion coefficients correspond to higher experimental graphene concentrations. In the low diffusion limit however, this relationship breaks down. We suggest that here the concentration of graphene in solution depends primarily on the separation efficiency of the initial LPE step.

REFERENCES

[1] Coleman, Accounts of chemical research, 46 (2012) 14
[2] Patil et al, The Journal of chemical physics, 149 (2018) 094702

FIGURES

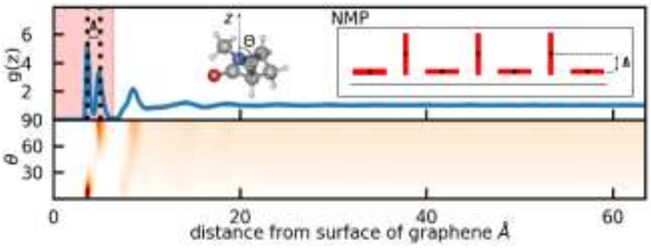

Figure 1: Position (top panel) and angle (bottom) distribution function for N-Methyl-2-Pyrrolidone (NMP) molecules as a function of distance from a graphene monolayer. The insert shows how the co-adsorption of NMP at two different angles results in the double-peak structure of the first solvation shell.

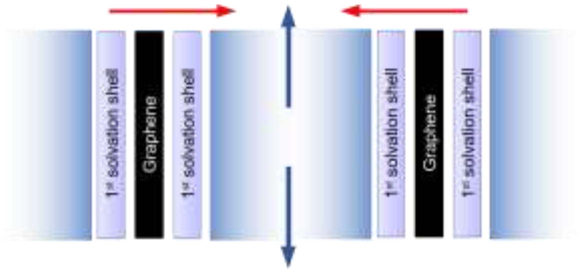

Figure 2: Re-aggregation model: The solvent molecules must diffuse out between two re-aggregating graphene layers. The parallel diffusion coefficient of the first solvation shell will determine the reaggregation efficiency.