

# Exfoliating Two-Dimensional Layered Materials: Solvent Interactions on Graphene and MoS<sub>2</sub> from First-Principles

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Liquid Phase Exfoliation (LPE) has emerged as an inexpensive and scalable candidate for the mass production of two-dimensional (2D) materials [1]. The particular choice of solvent is critical to achieving a high yield of monolayers; matching the surface tension of solvent and solute is the current guiding principle in the search for optimal solvents [2]. Yet this principle cannot be applied universally - in some cases the yield can be very low despite an excellent match between solute and solvent. As the atomic scale mechanism of the process is not well understood, a 'trial and error' experimental procedure is used to find the optimal solvent for a particular layered material.

While it is assumed that the solvent does not interact covalently with the solute, little else is known about the interaction between the two. Here we use density functional theory (DFT) to determine the adsorption configuration and binding energy of a variety of solvent molecules on two of the most popular 2D materials, namely graphene and MoS<sub>2</sub>. We show that, as expected, these molecules are physisorbed on the surface with little charge transfer between the two. Despite this, a significant charge rearrangement occurs at the interface (Figure 1).

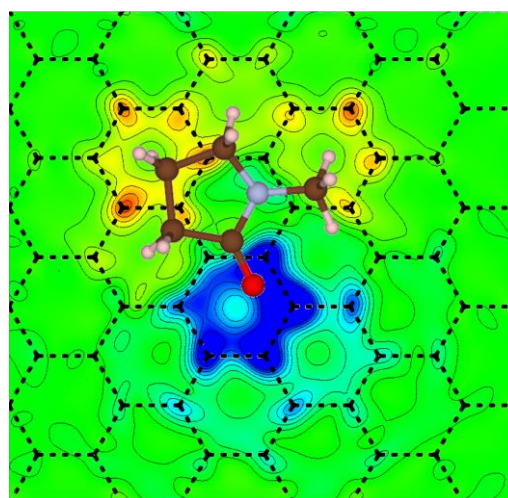
Furthermore, some graphene intercalation compounds (GICs) are known to spontaneously disintegrate into their constituent layers when mixed with polar solvents [3]. We show that the adsorption or intercalation of alkali metal atoms on a

graphene slab always increases the interlayer binding energy. As a result, the exfoliation of an intercalated graphene bilayer into its neutral components is not energetically favourable. Using an implicit solvation model, we show that this is true regardless of the properties of the solvent. However, the large solvation energy of charged graphene and metal ions is sufficient to overcome the increased binding energy of the intercalated bilayer so that it can be exfoliated into its charged components. We show how the exfoliation depends on the relative permittivity and surface tension of the solvent as well as on the concentration of the intercalated atoms.

## References

- [1] Hengcong Tao, et al., *Phys. Chem. Chem. Phys.*, 19 (2017), 921
- [2] Jonathan N Coleman, *Acc. Chem. Res.* 46 (2013), 14
- [3] Patrick Cullen, et al., *Nature Chemistry*, 9 (2017) 244

## Figures



**Figure 1:** Relative orientation of N-Methyl-2-pyrrolidone (NMP) adsorbed on graphene. The charge rearrangement is shown by a slice of the charge density difference after adsorption, taken 0.5 Å above the graphene plane.