What governs the "efficiency" of liquid phase exfoliation?

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Liquid phase exfoliation (PLE) has become an important top down production technique giving access to large quantities of nanosheets in colloidal dispersion. Importantly, this is a highly versatile technique that can be applied to numerous layered materials from graphite to transition metal dichalcogenides, *h*-BN, III-VI semi-conductors, hydroxides etc. All materials can be exfoliated in a similar way using aqueous surfactant or suitable solvents as stabilisers. However, the nanosheets in dispersion are extremely polydisperse with broad lateral size and thickness distributions. To narrow size and thickness distributions, liquid cascade centrifugation (LCC) has proven to be a powerful tool for efficient size selection yielding nanosheet dispersions with well-defined changes in their lateral dimensions and thickness.[1,2]

In spite of this progress, it has thus far been unclear which aspects govern the efficiency of exfoliation. In which way is the yield, nanosheet size and layer number dependent on the liquid medium? What is a good descriptor for the efficiency of LPE? What controls the efficiency of exfoliation?

In this talk, these fundamental questions will be addressed. About 15 different layered crystals with a range of structures, chemical compositions, crystallite shape and inter- and intra-layer bonding strengths were exfoliated by sonication and subjected to LCC size selection. In each fraction, nanosheet dimensions were quantified by statistical AFM analysis. Crucially we find that the nanosheet lateral size scales with the layer number as power law. This scaling can be used to determine the characteristic monolayer size for the different materials which can be regarded as quantitative measure for the exfoliation efficiency. Interestingly, we find that this parameter (in contrast to yield and relative population of nanosheets of a given size/thickness) is widely independent on the liquid used in LPE.

To understand this exfoliation behaviour, a simple non-equilibrium thermodynamics-based model was developed[3] predicting that the characteristic monolayer size is proportional to the ratio of in-plane-tearing/out–of–plane-peeling energies. By comparing the experimental data with the tearing/peeling ratio calculated from first principles, we find close agreement between experiment and theory suggesting that energy equipartition holds between nanosheet tearing and peeling during sonication-assisted exfoliation.

This means that the lateral size- thickness aspect ratio is based on intrinsic physical properties of the crystal that can likely not be overcome by attempting to fine-tune LPE in high energy processes. The model also allows to predict the exfoliation efficiency of unexplored materials based on computed elastic constants.

References

[1] Backes et al. *ACS Nano* (2016), 10, 1589–1601.

[2] Ogilvie et al. *2D Mater.* (2019), 6, 031002.

[3] Backes, Campi, …, Marzari, Coleman, O'Regan; *ACS Nano* (2019), in review.