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Correlation of van der Waals Binding Energy of Layered Materials and Their Bulk Modulus

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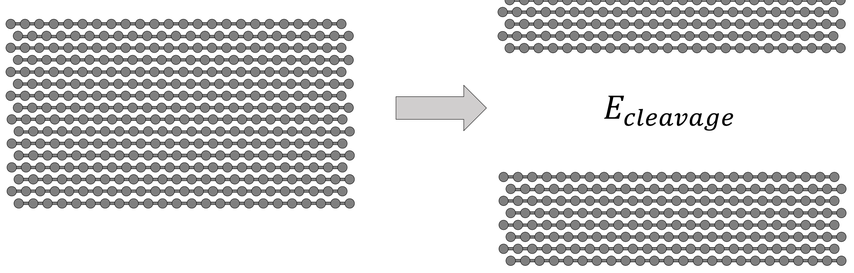
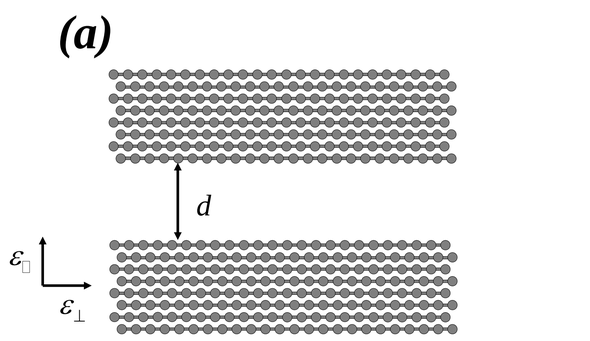
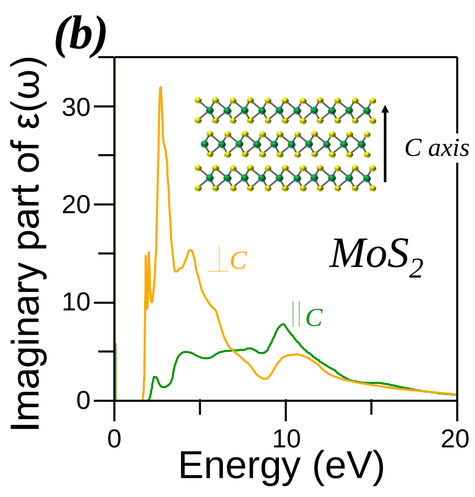


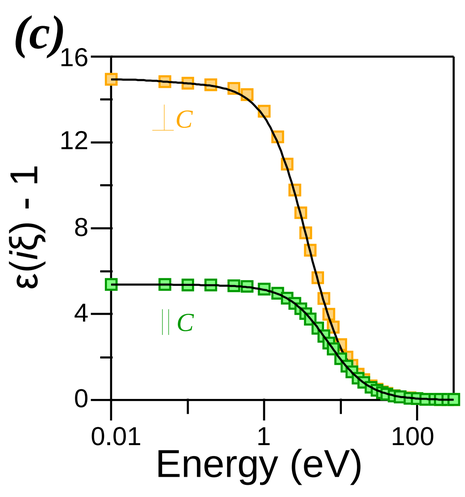
Introduction: The key to successful exfoliation of layered materials is relatively low binding energy that holds layers together. In non-polar layered materials, the interactions energy among the layers are dominantly van der Waals (vdW) interactions.

The energy that is required to split layered materials perpendicular to main crystallographic axis is known as cleavage energy. This quantity has rarely been measured for many layered materials despite its paramount importance to 2D materials' research. Advanced computational methods are able to calculate the cleavage energy but the outputs are not consistent. For instant, cleavage energy of hexagonal boron nitride (hBN) is found to be larger than graphite and MoS_2 by Jung et al. [1], whereas calculations by Björkman et al. [2] suggest the opposite trend. Here I argue that bulk modulus of the layered materials can be used to evaluate the cleavage energy of the layered crystals.

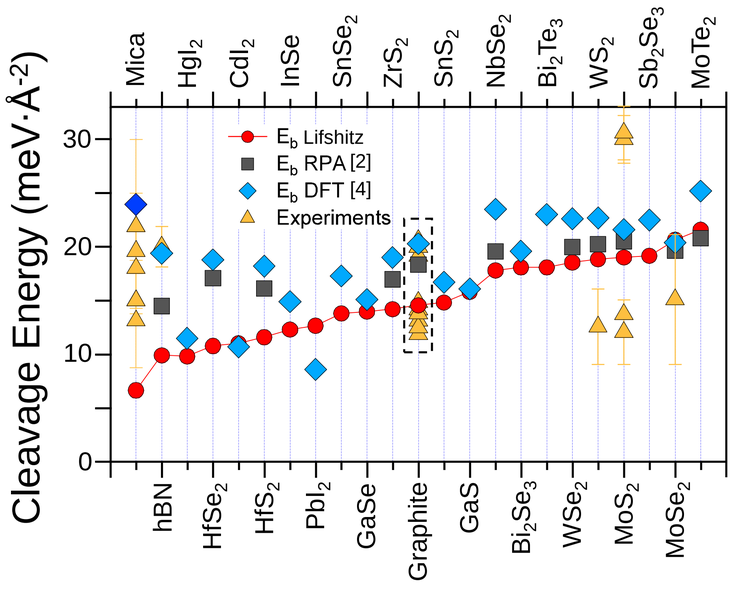


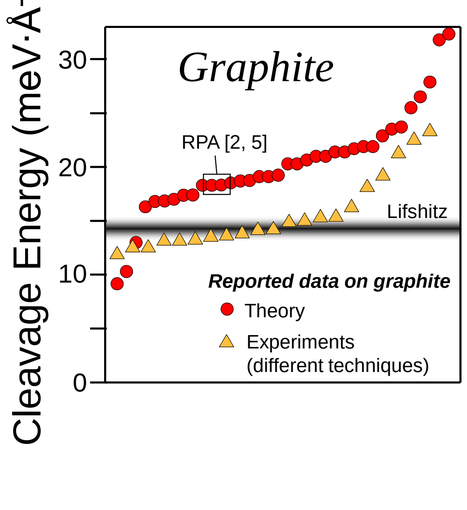
$$E_{vdW} = \frac{k_B T}{8\pi d^2} \sum_{n=0}^{\infty}{}' \int_0^{\infty} x \ln[1 - \frac{\sqrt{\varepsilon_{\perp}\varepsilon_{\square}} - 1}{\sqrt{\varepsilon_{\perp}\varepsilon_{\square}} + 1} e^{-x}] dx$$



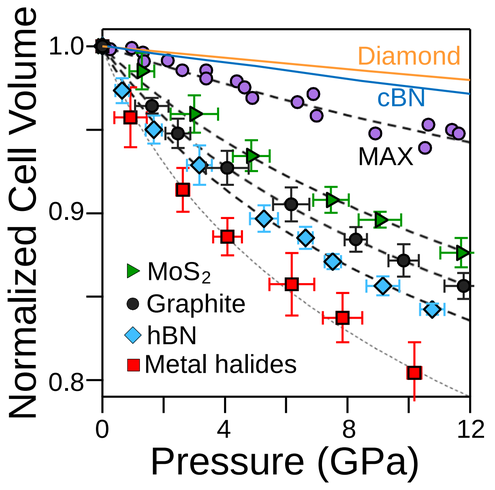


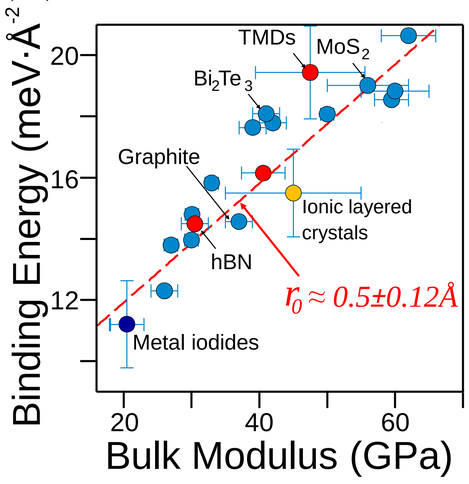
Lifshitz theory for vdW forces: vdW forces among materials can be computed using Lifshitz approach (a). This requires the dielectric functions of materials in a wide photon energy along different optical axes. There are few layered materials that such data are measured, for instance MoS_2 (b). The advantage of Lifshitz theory is that dielectric functions in imaginary frequencies are enough to compute vdW forces (c). Based on evaluating a large set of experimental data for different materials [3], an improved empirical model was developed to predict dielectric functions of materials using widely available physical constants. These functions was used to calculate Hamaker constants of layered materials.





Cleavage energy : Cleavage energy can be estimated from the calculated Hamaker constants provided that the vdW cut-off distance is known. For many liquids and solids this cut-off distance is about 1.65 ± 0.1 Å [3]. The vdW cleavage energy of several layered materials are then computed. For polar materials such as hBN, there are additional interactions that holding layers together. For graphite, the estimated cleavage energy matches many experimental data but it is lower than theoretical work. For non-polar TMDs, Lifshitz theory predicts similar cleavage energy as *ab initio* calculations do [2].





Assuming a L-J potential among atoms is valid and using third-order Birch-Murnaghan equation of state, one arrives to following relation between, cleavage energy and bulk modulus (K_0):

$$E_{cleavage} \approx \frac{K_0 r_0}{16}$$

Cleavage enegy vs. Bulk modulus: A linear relation between bulk modulus and cleavage energy of layered materials is predicted. Experimentally measured bulk modulus of more than 30 different layered materials (reported in literature) are compared to the computed binding energy, which confirms the presence of such linear relation. As it is expected, for polar layered materials such as hBN and HfS_2, non-vdW interactions must be taken into account for them to fall into the same line as other non-polar layered materials. This analysis clearly shows that the bulk modulus of layered materials are largely affected by the magnitude of the vdW interactions and subsequently their optical properties. A vdW gap (r_0) of 0.5 ± 0.12 Å is found which is in agreement with proposed values by Hu et al [6] for hBN and MoS_2.

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