Materials at the 2D Limit

The Objective: Two-dimensional (2D) materials are systems which have macroscopic lateral dimensions (reaching several millimeters in some cases) but have thicknesses on the nanometer scale. This allows them to both host a wide range of quantum behaviors – from superconductivity[1] to exotic excitonic states[2] - while also being large enough to integrate into devices. The objective of this activity is to make a 2D sample of MoS_2. These systems can be made by either a "bottom-up" approach, synthesizing the system one-layer-at-a-time (e.g., chemical vapor deposition or molecular beam epitaxy), or though a "top-down" approach, where a bulk material is thinned down to the atomic limit. This latter approach is often called the "scotch-tape" method, because the first iteration (and the version we'll use) used scotch-tape to pull apart the 2D materials.

The System: MoS_2 is one of the most widely studied members of a class of 2D materials called transition metal dichalcogenides (TMDCs). These materials have strong covalent bonds between atoms in the same layer, but only weak van der Waals forces *between* layers, which makes exfoliating them down to the single-layer limit possible. MoS_2 also displays remarkable thickness dependent properties; the vibrational modes (which we can measure with Raman spectroscopy) change as the sample gets thinner, and fluorescent emission (forbidden in the bulk crystal) becomes extremely strong in thin samples because of changes to the band structure.

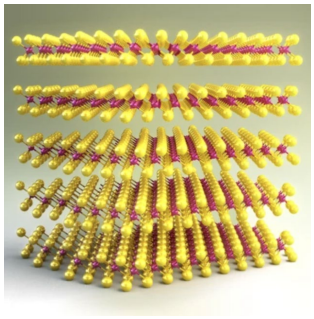

Figure 1 – MoS_2 in its bulk form has weak van der Waals interactions between layers.

The Hardware: The hardware for making our 2D samples is simple: scotch tape, a crystal of MoS_2, and a substrate we want to exfoliate our sample on to. Every 2D material group has their own preferred brand of tape; for the sake of tradition, we'll stick with the original scotch tape used by Andre Geim to form graphene monolayers. We'll compare two substrates – microscope slides (make from amorphous SiO_2), and silicon chips with a few hundred nanometers of SiO_2 on the surface. In both cases the surface material is the same, but we'll hopefully see the optical properties are very different. We'll use a small digital microscope to image the 2D materials at the surface.

To explore the material in more detail, we'll use a Raman microscope. Raman spectroscopy uses an intense monochromatic laser focused down to a small spot to characterize vibrations in a sample; a small fraction of incident photons will excite a vibration in the sample, losing a characteristic amount of energy. We can use this to see changes in the thickness of the samples. However, this instrument can also measure fluorescence spectra; bulk MoS_2 does not emit light, but if we are able to thin MoS_2 down to the few-layer limit, we will see intense fluorescence. In fact, if we can reach the limit of a single MoS_2 layer, we'll observe extremely bright emission wit ha narrow peak lineshape.

[1] Yuan Cao et al., "Unconventional Superconductivity in Magic-Angle Graphene Superlattices," *Nature* 556, no. 7699 (April 2018): 43–50, https://doi.org/10.1038/nature26160.
[2] Zefang Wang et al., "Evidence of High-Temperature Exciton Condensation in Two-Dimensional Atomic Double Layers," *Nature* 574, no. 7776 (October 2019): 76–80, https://doi.org/10.1038/s41586-019-1591-7.

The Experiments: There are three parts to this activity: making the 2D samples, initial characterization with optical microscopy, and detailed characterization with Raman microscopy.

(1) Exfoliation: First, we need to thin out our MoS_2 to the 2D limit. The QR code on the right will link to a youtube video demonstrating the process. The summary is: keep making copies with the scotch tape until the MoS_2 is barely visible, then apply the tape to the substrates.

Watch a demo of the exfoliation method using this QR code

Questions: Why does this method work? How scalable is this approach?

(2) Optical Imaging: Make MoS_2 samples on the two substrates (glass slide, silicon chip), and image these under the microscope. Identify promising looking flakes for imaging with the Raman microscope

Questions: Why are different flakes different colors? Is this consistent across substrates (microscope slide vs. Si/SiO_2 chip)?

(3) Raman Imaging: With some flakes identified for further study, we'll measure the Raman response for several different laser excitation wavelengths. We can use previously reported values to estimate the thickness of these flakes[3].

Questions: How reliable is this method for determining thickness, and how could you improve it? What's the thinnest flake you were able to find?

Further Reading:

Y-C Lin *et al*, "Recent Advanced in 2D Material Theory, Synthesis, Properties, and Applications", *ACS Nano*, **17**, 9694 (2023)

[3] Hong Li et al., "From Bulk to Monolayer MoS2: Evolution of Raman Scattering," *Advanced Functional Materials* 22, no. 7 (2012): 1385–90, https://doi.org/10.1002/adfm.201102111.