

Wrapping Microdroplets with Two-Dimensional Materials

CNF Project Number: 900-00

Principal Investigators: Paul L. McEuen^{1,2}, Itai Cohen^{1,2}, Jiwoong Park^{3,4}

**Users: Kathryn L. McGill¹, Michael F. Reynolds¹, Marc Z. Miskin^{1,2},
Maritha Wang^{3,4}, Hui Gao^{3,4}, Kibum Kang^{3,4}**

Affiliations: 1. Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca NY, USA; 2. Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca NY, USA; 3. Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY, USA; 4. Department of Chemistry, Institute for Molecular Engineering, and James Franck Institute, University of Chicago, Chicago IL, USA

Primary Sources of Research Funding: Cornell Center for Materials Research with funding from the NSF MRSEC program (DMR-1719875), Air Force Office of Scientific Research (AFSOR) Multidisciplinary Research Program of the University Research Initiative Grant FA2386-13-1-4118

Contact: plm23@cornell.edu, klm274@cornell.edu, mfr74@cornell.edu

Primary CNF Tools Used: Autostep i-line stepper, Oxford 81 etcher

Abstract:

We present experiments demonstrating the wrapping of microscopic oil droplets by two-dimensional (2D) materials. We show that 2D materials such as graphene and molybdenum disulfide (MoS_2) wrap microscopic liquid drops in the same ways in which millimeter-scale drops were wrapped by thin elastic sheets [1,2].

Summary of Research:

Wrapping fluid droplets with thin elastic sheets has been used to perform capillary origami [3] and as a technique to measure bending moduli [4] of thin films. In the case where the bending energy of the sheet is much smaller than the surface tension of the droplet, the minimization of surface energy by wrapping and the inability for a planar sheet to take on Gaussian curvature determine the shape. Previous experiments include geometric wrapping patterns of droplets [2] and wrinkling of sheets on droplet surfaces [5]. Here we perform analogous experiments on the wrapping of oil droplets in water with the thinnest possible materials: one-atom-thick graphene and three-atom-thick MoS_2 .

We begin by photolithographically patterning 2D materials into a variety of simple shapes using the GCA AutoStep 200 i-line wafer stepper and the Oxford etchers at the Cornell NanoScale Science and Technology Facility. We use commercially available graphene on copper (Grolltex) and transfer it onto glass coverslips using a poly(methyl methacrylate) (PMMA) support layer. Our MoS_2 samples are grown onto glass coverslips via metal-organic chemical vapor deposition (MOCVD) by collaborators in Jiwoong Park's group at the University of Chicago, and we cover them in a protective layer of

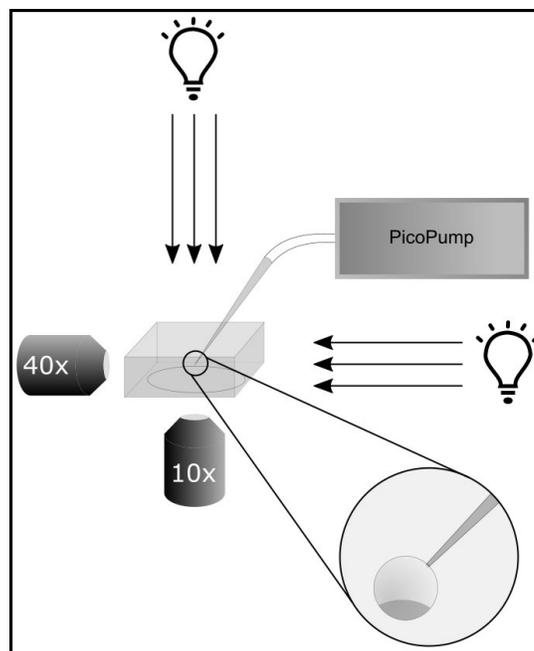


Figure 1: Schematic of setup. Inset shows Fluorinert drop with 2D material wrapping from the bottom.

PMMA during fabrication. After patterning, we etch through the PMMA/MoS₂ or graphene to define our features. We then remove the PMMA and release the graphene or MoS₂ from the glass substrate with a dilute hydrofluoric acid etch.

The experimental setup is shown schematically in Figure 1. The substrates containing the 2D material sheets are placed in a home-built cuvette filled with deionized water. Using an electronic micromanipulator (Sensapex), we position a glass micropipette filled with Fluorinert FC-70 (3M), an oil that is both denser than and index-matched to water, over the graphene/MoS₂ sheets. Droplets are formed by applying pressure spikes (Picopump, World Precision Instruments) to the micropipette, then lowered onto the 2D material sheets for pick up. We then use suction to shrink the droplet until it is completely wrapped by the 2D sheet. Simultaneously, we record the bottom and side views of the process using an inverted microscope and side-view objective, respectively.

Once we pick up the sheets, we use both the side and bottom views to simultaneously watch the wrapping process. Figure 2 shows a time series of images from both cameras as a circular MoS₂ sheet wraps a Fluorinert droplet. Frames 1 and 2 show the initial deflection of the droplet from a spherical shape due to the MoS₂ sheet. Frame 3 shows a triangular-wrapped shape, one of the typical wrapping geometries for circular sheets [2], before the shape is distorted by vacuum removal of Fluorinert in frames 5 and 6.

For circular sheets, we see triangular prisms, shown in Figure 3A, and “empanada” wrapping states. For square sheets, we see square “turnover” wrapping patterns – where the four corners are folded to the center, shown in Figure 3B. For triangular sheets, as with the circular ones, wrapping corresponds roughly to triangular prisms, shown in Figure 3C. Overall, we find that wrapping geometries are similar to those in Ref. (2) and are determined by the initial shape of the 2D material sheet.

This demonstration indicates a new route for making 3D geometries out of 2D materials by drawing on an existing literature of droplet wrapping with sheets, and it suggests the possibility of using 2D materials to perform wrapping at more complicated fluid interfaces, or to controllably form 3D microstructures. Future work includes new patterns to demonstrate capillary origami folding with 2D materials as well as wrapping droplets with devices with optical, electronic, and/or magnetic components.

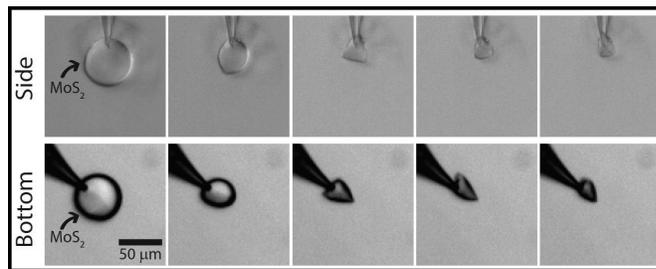


Figure 2: (top) Time lapse of Fluorinert droplet wrapping by MoS₂, side view; (bottom) Time lapse of the same droplet wrapping, bottom view.

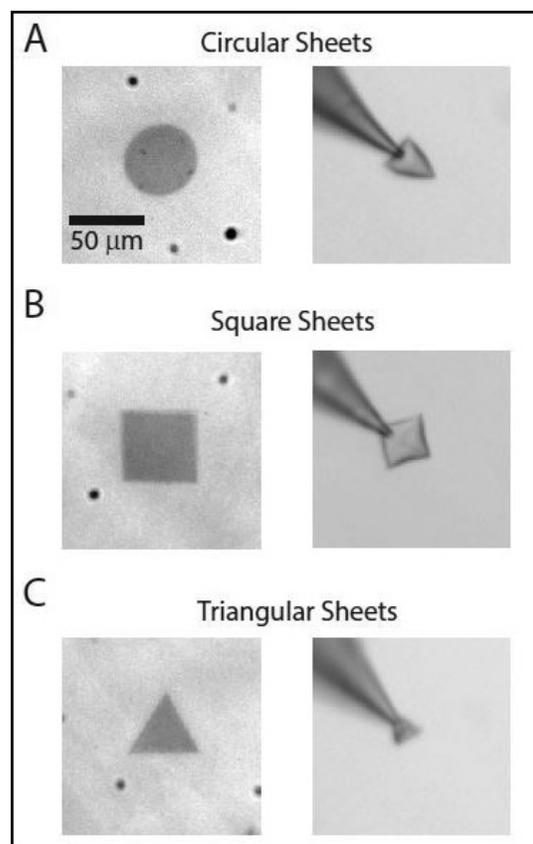


Figure 3: Final wrapped states for various sheet geometries.

References:

- [1] D. Kumar, J. D. Paulsen, T. P. Russell, N. Menon, *Science*. 359, 775 (2018).
- [2] J. D. Paulsen et al., *Nat. Mater.* 14, 1206-1209 (2015).
- [3] G. McHale, M. I. Newton, N. J. Shirtcliffe, N. R. Gheraldi, *Beilstein J. Nanotechnol.* 2, 145-151 (2011).
- [4] J. Bae, T. Ouchi, R. C. Hayward, *ACS Appl. Mater. Interfaces*. 7, 14734-14742 (2015).
- [5] J. Huang et al., *Science*. 317, 650-653 (2007).