Measuring and Modeling Liquid-Filled Nanobubbles Trapped by 2D Materials

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Layered systems of van der Waals (vdW) bonded two-dimensional (2D) materials are widely explored for new physics and devices. In many cases, 2D atomic layers are transferred on a foreign substrate, including other 2D materials. It has been extensively reported that nanometer-scale interfacial bubbles form spontaneously after the transfer [1]. So far, there is no consensus on whether these nanobubbles are filled by liquid, solid, or gas.

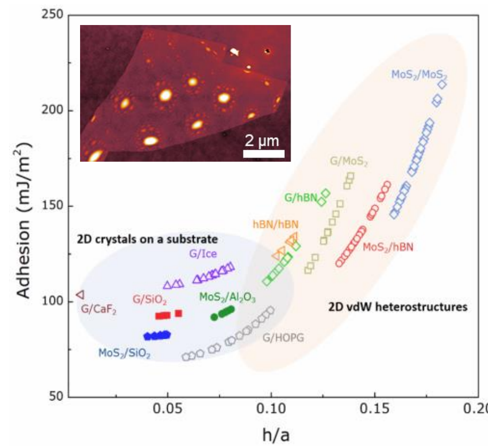

Figure 1. Adhesion energy for various 2D material interfaces with respect to the aspect ratio of the confined bubble, where *h* and *a* represent the height and radius of the bubble, respectively. Data shown with solid markers are taken from experiments performed in this study, and data with no fill are taken from the literature. The inset is an AFM image of graphene on SiO_2 with bubbles shown as white circular regions.

We have carried out time-lapse atomic force microscopy (AFM) scans on nanobubbles trapped between graphene and SiO_2 (Fig. 1 inset). The bubbles deflate slower than ideal-gas-filled 2D membranes over a course of 92 days indicating that liquid is likely trapped under the 2D membrane [2]. We therefore develop a theoretical framework built upon the membrane equations for a thin, elastic membrane trapping incompressible liquid to form interfacial bubbles. Our final analytical solution suggests that adhesion between the 2D material and its substrate is related to the fourth power of the aspect ratio of the blister, which is a constant irrespective of the blister diameter. Our model is applied to estimate the adhesion energy of various 2D material interfaces using the experimentally measured aspect ratios of the bubbles (Fig. 1). Good agreement between the estimated adhesion energies of graphene-SiO_2 and MoS_2-SiO_2, and those reported in the literature substantiates our model. In conclusion, liquid-filled nanobubbles trapped by 2D materials can be used as a simple but generic metrology for the adhesion of 2D materials.

[1] E. Khestanova, F. Guinea, L. Fumagalli, A. K. Geim, I. V. Grigorieva, *Nat. Commun.* **7**, 12587 (2016)
[2] D. Lloyd, X. Liu, J. W. Christopher, L. Cantley, A. Wadehra, *et al*., *Nano Letters* **16**, 5836–5841 (2016)
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$$\frac{h}{a} = \left(\phi \frac{\Gamma - \gamma_w(\cos\theta_m + \cos\theta_s)}{E_{2D}}\right)^{\frac{1}{4}}$$

Equation S1. Relationship between aspect ratio of the bubble (*h*/*a*) and adhesion energy between the 2D material and its substrate, where Γ is adhesion energy, γ_w is the surface tension of water, θ_s and θ_m are the water contact angles of the substrate and the membrane, respectively, E_{2D} is the in-plane elastic stiffness, and ϕ is a dimensionless coefficient that is a function of the Poisson's ratio of the 2D material.

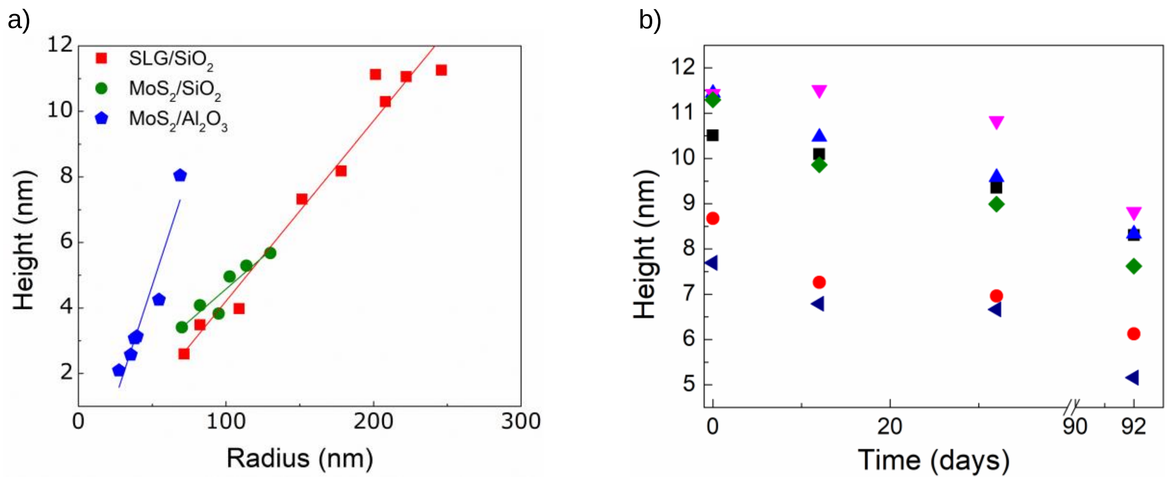

Figure S1. (a) The relationship between the height and radius of the bubbles found at various 2D material interfaces is linear. (b) The heights of six graphene nanobubbles tracked over 92 days. The radius remains constant.