1 Direct Measurement of the Contents, Thickness, and Internal 2 Pressure of Molybdenum Disulfide Nanoblister

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5 **ABSTRACT:** Nanoblister have attracted attention due to their ability to
6 controllably modulate the properties of two-dimensional materials. The
7 accurate measurement or estimation of their properties is nontrivial and
8 largely based on Hencky's theory. However, these estimates require *a*
9 *priori* knowledge of material properties and propagate large errors. Here
10 we show, through a systematic atomic force microscopy study, several
11 strategies that lead to vastly enhanced characterization of nanoblister.
12 First, we find that nanoblister may contain both liquid and gas, resolving
13 an ongoing debate in the literature. Second, we demonstrate how to
14 definitively determine the membrane thickness of a nanoblister and show
15 that Hencky's theory can only reliably predict membrane thicknesses for
16 small aspect ratios and small membrane thicknesses. Third, we develop a
17 novel technique to measure the internal pressures of nanoblister, which
18 quantitatively agrees with Hencky's theory but carries a 1 order smaller
19 propagated error.

20 **KEYWORDS:** nanoblister, MoS₂, contents, thickness, internal pressure, atomic force microscope

21 **N**anoblister are layers between one and several atoms
22 thick which delaminate off two-dimensional (2D)
23 materials such as graphene or molybdenum disulfide (MoS₂)
24 into a taut bump that may contain liquid or gas. Traditionally,
25 they are considered undesirable,^{1–4} as they are inadvertently
26 produced during the fabrication of atomically flat and pristine
27 2D materials, for example, during the transfer of exfoliated 2D
28 materials.

29 In recent years, however, nanoblister have attracted
30 substantial research interest in their own right, both for
31 fundamental understanding and for deployment in onward
32 applications. The ability to *controllably* pattern 2D materials
33 with defects allows the optical and mechanical properties of 2D
34 materials to be modulated, carrying implications in nonlinear
35 optics,⁵ energy storage,^{6,7} and quantum emission.^{8–10}
36 Furthermore, the detailed characterization of nanoblister
37 offers a simple way to calculate fundamental properties of
38 the originating material, such as adhesion energy,^{11,12} gas
39 transport coefficients,¹³ or interlayer stresses between individ-
40 ual layers¹⁴ or between different types of 2D materials.¹⁵

41 One of the chief bottlenecks toward designing or engineer-
42 ing 2D heterostructures or devices utilizing nanoblister is in
43 the difficulty of accurately measuring mechanical properties.
44 Let us give two prominent examples. First, the attempt to
45 estimate the work of adhesion between films of 2D materials
46 has fissured into two camps—one assumes nanoblister

contain only gas,^{16–20} and another assumes they contain 47
only liquid.²¹ Some in the latter camp suggest²¹ that the more 48
widely used assumption that the blisters contain gas leads to a 49
systematic underestimation of adhesion values. It is clear that 50
an authoritative estimate of adhesion requires a technique to 51
discern the identity of the nanoblister's contents. 52

Second, the bending and stretching energy of a nanoblister is 53
sensitive to the precise number of layers that comprise the 54
blister's membrane, but the layer number is unfortunately 55
challenging to determine. Typical approaches to measure 56
membrane thicknesses include optical transmittance, photo- 57
luminescence, or Raman signatures of cleaved membranes^{22–24} 58
through whole films of 2D materials. However, these 59
approaches lack the capability to resolve thicknesses of blisters 60
larger than a few layers, and are diffraction limited, precluding 61
the ability to probe individual nanoblister. 62

In this Letter, we demonstrate a path toward overcoming 63
these challenges by using the unique modalities of atomic force 64
microscopy. 65

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Figure 1. Deflation of nanoblister after desiccation. AFM height images are collected in air for the samples as prepared (a, c) and after storage for a week (b, d). Contour lines of the original blisters in parts a and c are shown by the black lines in parts b and d, respectively, which are produced with a thresholding algorithm. Large blisters were found to have deflated after a few days. (e) Cross-sectional profile at the white lines shown in parts a and b. (f) Cross-sectional profile of the horizontal white lines in parts c and d. Scan size: $20\ \mu\text{m} \times 20\ \mu\text{m}$ for parts a and b; $8\ \mu\text{m} \times 8\ \mu\text{m}$ for parts c and d. Height scale: 500 nm for parts a and c; 50 nm for parts b and d.

Figure 2. Pits on bulk MoS_2 form when nanoblister ruptures. (a) An AFM height image in contact mode showing pits with circular contour, scan size $20\ \mu\text{m} \times 20\ \mu\text{m}$, height scale 10 nm. (b) Cross-sectional profile at the position shown in part a. The pit is two atomic layers thick. (c) The distribution of pit depths ($N = 106$) formed during the electrochemical reactions. (d–f) Schematic of pit formation. Blister inflates and become taut with the introduction of hydrogen (d), but when the pressure exceeds a threshold, the blister ruptures (e) and the top of the membrane peels over (f).

microscopy (AFM), to resolve the internal composition and membrane thicknesses of MoS_2 nanoblister in an unambiguous fashion.

We generate nanoblister on MoS_2 using a similar technique to that reported in ref 7—electrochemically splitting an aqueous solution containing 10 mM Na_2SO_4 using bulk MoS_2 as the cathode. Immediately after fabrication, we removed the solution and characterized the nanoblister with

AFM in air, before storing them in a desiccator for several days. Parts a and c of Figure 1 show representative examples of nanoblister fabricated with electrochemical water splitting—in Figure 1a, the blister has a height of $h = 290\ \text{nm}$ and a footprint radius of $a \sim 4\ \mu\text{m}$, while, in Figure 1c, $h = 160\ \text{nm}$ and $a \sim 2\ \mu\text{m}$. In each scan, the blister is surrounded by several smaller blisters with diameters of several hundred nanometers. The largest blister in each of Figure 1a and c deflates after

Figure 3. Rupturing nanoblister with an AFM tip. Here we focus on two nanoblister, #1 and #2, as seen in height (a) and phase (c) images. After rupturing each blister, we observe a dark (i.e., lower than the surface average) pit surrounded by irregular but flat objects reminiscent of the ruptured membrane of the nanoblister (b, d). (e and f) Cross-sectional profiles of blisters #1 and #2 before and after rupturing them with the AFM tip. The solid lines are least-squares fits to spherical caps. (g) A schematic of a delaminated blister after rupture with an AFM tip, for blisters mainly filled with gas (upper panel) and a blister filled with both liquids and gases (lower panel). In parts a–d, the scan size is $4 \mu\text{m} \times 4 \mu\text{m}$, the height scale is (a) 100 nm and (b) 10 nm, and the phase scale is 20° for parts c and d.

desiccation for a week. More surprisingly, the smaller blisters nearby do not deflate but persist for 6 months or more.

Interestingly, we observed the presence of numerous pits in the AFM images, Figure 2a. A cross-section of one of these pits shows that one side of the object is elevated beyond the background substrate, while the other side of the object—i.e., the pit—is recessed below the background substrate. Furthermore, pit depths are quantized. Of a random sampling of 106 pits, we found that about 40% possess a depth of ~ 1.3 nm, corresponding to two atomic layers of MoS₂. Overall, approximately 95% of the 106 pits possess a depth of up to four atomic layers of MoS₂. We also found that the pit depths were independent of their lateral radii.

We hypothesize that the pits originate from ruptured nanoblister, as illustrated schematically in Figure 2d–f. During the electrochemical reaction, it is likely that gas, water, or both infiltrate between layers of MoS₂, causing a taut nanoblister to delaminate from the substrate and inflate. Since external energy is continuously being supplied by the electrode, it is reasonable to assume that gas and water might continuously enter the nanoblister, until the point that its internal pressure cannot mechanically support its contents, leading to its rupture. By symmetry, the tensile stress on the membrane, when projected onto the plane of the MoS₂ substrate, is directed radially outward with respect to the center of the nanoblister's radius of curvature. Thus, upon rupture, the nanoblister's membrane should fold outward, creating a pit where the nanoblister originally stood. Qualitatively similar structures have also been found by Berkelaar et al.²⁵ during the evaporation-induced rupture of salt-covered surface nanobubbles.

To confirm that the pits originate from nanoblister that rupture during the electrochemical process, we use an AFM tip to deliberately rupture intact nanoblister. We select an AFM cantilever with a relatively sharp tip radius of about 2 nm (Supporting Information Figure S2) and, performing the experiment in air, move the AFM tip toward randomly selected

blister at a velocity of $1 \mu\text{m/s}$. (This capability is widely available in most AFMs through a force spectroscopy module.) We indeed find that a deliberately ruptured nanoblister creates qualitatively similar pits to those already found across the substrate.

Our technique of rupturing nanoblister allows us to resolve the internal composition of the nanoblister. In Figure 3a, we show two blisters, marked #1 and #2, which possess similar aspect ratios h/a of 0.144 and 0.122, respectively. Here h is the height and a the footprint radius of the nanoblister. We rupture each nanoblister with a sharp AFM tip and then immediately image in air with AC mode (also known as tapping mode) AFM.

This procedure produces two distinct behaviors. Upon rupture with an AFM tip, some nanoblister, such as nanoblister #1, respond by spreading their membranes radially outward and leaving behind a flat and bare pit, as schematically illustrated in Figure 3g. As imaging is performed in air and no significant residue is observed in the vicinity of nanoblister #1, we surmise that it mainly contains gas. The difference in the height image between the pit and the background substrate is two atomic layers—as earlier argued—implying the membrane is two layers thick.

In contrast, when blister #2 was ruptured with the AFM tip, the membrane was also seen to collapse upon rupture, yet a new object of about 170 nm in height emerged on top of the region where the original nanoblister once stood. Interestingly, the height of the new object is $\sim 4\times$ larger and its volume is $\sim 2\times$ larger than the height and volume of the original blister, respectively.

Further characterization allows us to surmise that nanoblister #2 contains liquid. First, phase channel AFM imaging (Figure 3d) allows us to distinguish between the background MoS₂ and softer objects. On nanoblister #1, only a MoS₂ membrane with a modest phase contrast with the bulk MoS₂ is produced by rupturing the membrane, but when nanoblister #2

Figure 4. Measured layer number of nanoblister by rupturing with the AFM tip. (a) Measured membrane thickness n_{AFM} versus the theoretical thickness predicted by Hencky theory, n_{theory} . (b) Measurement error $|n_{\text{AFM}} - n_{\text{theory}}|/n_{\text{AFM}}$ versus height/radius ratio h/a .

is ruptured, one finds a new object that is mechanically distinct from MoS_2 . Second, a cross-sectional profile of the object left behind after rupturing blister #2 (see Figure 3f) is well-fitted to a spherical cap, indicating the object possesses an energy minimizing interface. Since images are performed in air, we can finally surmise that the object is nongaseous, i.e., a water microdroplet or a water microdroplet encapsulating gas. Third, when we left the system to stand overnight, a soft object formed after rupturing a blister similar to blister #2 was found to have shrunk considerably in height and size by the next day, indicating that it was an evaporating water droplet; see Figure S3.

Although careful characterization shows the presence of liquid in nanoblister (Table S1), as illustrated schematically in Figure 3g, it is not immediately clear how liquid accumulates between layers of MoS_2 . It is known that, in the presence of bias, sodium ions can modify parts of the crystalline structure of MoS_2 to the form Na_xMoS_2 .²⁶ Being no longer purely two-dimensional, the modified crystalline structure introduces in-plane compressive stresses that produce cracks across the MoS_2 .²¹ In previous work, An et al.⁷ found that applying bias to highly ordered pyrolytic graphite also produces a similar effect. Additionally, we observe in our experiments that nanoblister tend to form close to the terraces of MoS_2 layers (Figure S1), which are lines of structural weakness. We therefore hypothesize that the applied bias during electrolysis applies sufficient compressive stress to both overcome the work of adhesion and to delaminate the substrate. Due to ultralow friction between water and atomically flat 2D materials,^{27,28} water may seep through the first few layers of MoS_2 through the terraces of MoS_2 , the edges of which are untethered to the bulk. This hypothesis may explain why the water droplet produced by puncturing nanoblister #2 (see Figure 3) turns out to be even larger in volume than the nanoblister itself: because water is not necessarily localized within the nanoblister but may seep between atomic layers of MoS_2 . Finally, we note that we have not discerned the identity of the liquid in our experiments. Here we are reasonably sure that the liquid is water, since the working substrate is immersed in liquid, and no other chemical species melts at

room temperature. However, if so desired, more sophisticated AFM force measurements are capable of discerning the identity of the liquid. Immersed liquids adjacent to solid surfaces exhibit either a short-ranged ($\sim\text{nm}$) repulsion or attraction,^{29,30} while ionic liquids with relatively large molecules can present discrete steps over a distance of several nanometers.^{31–34}

Our results therefore show that nanoblister may contain both water and gas, and even both, contrary to the assumptions of previous studies in the literature. Because estimates of work of adhesion of materials like graphene and MoS_2 vary considerably depending on what the nanoblister are assumed to contain, our method provides an important step toward a reproducible and authoritative measurement of the mechanical properties of 2D materials.

We next focus on resolving the adhesion energy of nanoblister that are unambiguously known to contain liquid, using the model of Sánchez,

$\Gamma = \frac{E_{2D}h^4}{\Phi a^4} + \gamma_w(\cos \theta_m + \cos \theta_s)$.²¹ For a gas-filled blister, the term containing γ_w is omitted. Here, h and a are defined as above, γ_w is the surface tension of water (72 mN/m), and θ_s and θ_m are the water contact angles of the substrate and the membrane ($\theta_s = \theta_m = 69^\circ$ for freshly cleaved MoS_2 in this case). Here, we take the dimensionless quantity $\Phi = 1.2$ in the weak shear limit for the frictionless membrane–substrate interfaces²¹ (Figure S4 shows this assumption is justified, as MoS_2 are easily unpinned from the bulk substrate). For multilayered membranes, $E_{2D} = Ent$, where E is Young's modulus for bulk MoS_2 (270 GPa), n is the layer number, and t is the thickness of the monolayer MoS_2 (0.65 nm).³⁵ The adhesion energy was estimated as $\Gamma = 180 \pm 30 \text{ mJ/m}^2$ based on the parameters of blisters measured from AFM scans. These results yield an adhesion energy of $\Gamma = 178 \pm 18 \text{ mJ/m}^2$ from the nanoblister trapped between a monolayer MoS_2 on MoS_2 substrate, consistent with previous studies.^{15,21}

Reliable estimates of the mechanical properties of nanoblister hinge on an accurate estimation of the membrane thickness, which is unfortunately scarce. To circumvent this limitation, experimental estimates typically exploit a theory devised by Hencky, which considers how a thin, clamped

Figure 5. Improving on the Hencky technique of estimating the internal pressure of nanoblister. (a) When a nanoblister is indented with a blunt AFM tip, the indentation force varies proportionally with the indentation distance until the tip is recessed approximately ~ 25 nm into the elastic membrane. The gradient of this linear regime, which we denote Ω , has the units N/m and can be interpreted as an elastic spring constant. (b) Using our experimental measurements of Ω , h , a , and t , we systematically compare the predictions of internal pressure that arise from Vella's scaling theory, $\Delta p_v = \Omega/\pi R$, and the classical Hencky prediction, $\Delta p_H \sim \text{Ent}^3/a^4$. The consistency of the two approaches is justified from the fact that the experimental points collapse into a line in the dimensionless axes h^3/a^3 and $a\Delta p_v/\text{Ent}$. (c) While the absolute values of internal pressure predicted by the Hencky and Vella models agree to a reasonable degree, note how the propagated measurement errors are substantially larger in the Hencky measurements as compared to the estimates based on Vella's theory.

elastic membrane responds to a uniform loading perpendicular to the plane of the membrane. Then, the thickness of the membrane (in atomic layers) can be expressed as $n = \frac{\Phi a^4}{\text{Ent}^4} (\Gamma - \gamma_w (\cos \theta_m + \cos \theta_s))$.²¹ Physically, a uniform loading assumption is only truly realistic for a liquid-filled blister, since the loading originates from hydrostatic stress. For a gas-filled nanoblister, one should instead work from the assumption of a constant internal pressure.¹⁹ Fortunately, this assumption has only a marginal effect, as converting between the two formulations requires only a slight change of a numerical prefactor.⁷ The appeal of this technique is that it allows one to estimate the layer number n of a nanoblister from aspect ratio alone, since all other variables are known. However, despite its wide usage,^{21,36} we are not aware of a previous study in which the validity of Hencky's aspect ratio estimate has been rigorously tested. The ability to measure membrane thicknesses that we show in this paper affords us an opportunity to finally test the widely used Hencky estimate.

In Figure 4a, we show numerous nanoblister whose aspect ratio h/a and layer number n have both been resolved with atomic force microscopy by imaging and then poking them with an AFM tip. Nanoblister mainly filled with gas are marked in green, and nanoblister containing both liquid and gas are marked in red. To compare against the theoretical prediction, we plot the experimentally measured membrane thickness n_{AFM} against the membrane thickness implied by Hencky theory, n_{theory} . Surprisingly, we find good agreement between the Hencky theory and the AFM measurement when the nanoblister has membrane thicknesses below 4 layers.

A closer inspection, however, reveals that the Hencky theory substantially overestimates the true membrane thickness (i) when the membrane thickness exceeds 4 layers and (ii) when the aspect ratio h/a is large. Figure 4b shows the percentage error of the measurements. At small aspect ratios below 0.17, the percentage error is approximately constant (with some scatter) between 10 and 30% but abruptly diverges to 80% for a large aspect ratio of 0.22. These findings suggest that, while the Hencky estimate is reasonably accurate in most cases, it is imperfect and should be used cautiously in the limit of large membrane thickness or large aspect ratio.

Due to potential applications in energy storage and high pressure chemical nanoreactors, among others, there is

significant interest in knowing what kind of internal pressures the contents of nanoblister are subjected to. To a first approximation, these pressures must be formidable. For example, a gas bubble with a radius of 100 nm and surface tension of 72 mN/m possesses an internal Laplace pressure of several atmospheres. Due to added mechanical support from the nanoblister's membrane, an equivalent volume of gas in a nanoblister would have a much higher pressure.

Estimates of the internal pressure of nanoblister nearly invariably rely on the Hencky formula $\Delta p = \frac{\eta \text{Ent}^3}{a^4}$, where η is the shear coefficient and E , t , h , and a are defined above. Of these input variables into Hencky's formula, only h and a can be resolved easily by typical techniques used to characterize nanoblister. η is nontrivial to measure, while an estimate of n , as we mentioned earlier in this paper, can carry errors as large as 80% with Hencky theory.

Here we offer an alternative approach whose inputs avoid the uncertainty that comes with having to know *a priori* the mechanical properties of the material. When an AFM tip indents onto the nanoblister, the interaction force is dynamically captured based on the cantilever's instantaneous deflection. A typical example is shown in Figure 5a. The curve is read from right to left. Initially, the AFM tip descends toward the nanoblister's membrane; as it experiences no physical obstacle, no force is measured. As it comes into contact, the force increases linearly, before abruptly ending. In the case of the nanoblister shown in Figure S4, this point happens when the indentation distance is about half the nanoblister's height. Then, the force curve shoots sharply upward, indicating that the tip and membrane are now in contact with the underlying bulk substrate. Note that this procedure does not rupture the membrane, as the tip is blunt; a typical curve for a sharp AFM tip which does rupture the membrane is provided in the Supporting Information (Figure S5).

For any sufficiently small indentation, the force delivered by the indenter will vary linearly with the indentation length, $F \sim k\delta$. This principle has long been used to measure the osmotic pressures of viruses³⁷ and yeast.³⁸ Surprisingly, the linear regime can sometimes sustain longer than expected. For a pressurized elastic shell, Vella et al. find that, when $\delta \gg t_e$ (t_e is the thickness of the elastic membrane), the force follows $F \sim$

$k\delta = \pi\Delta p R\delta$, where π is the ratio of a circle's circumference to its diameter, Δp is the pressure, and R is the radius of a pressurized elastic shell.³⁸ From the AFM force curve in Figure 5a, we recover the force compliance of the nanoblisters by calculating the gradient of the linear regime marked in orange; this recovers the gradient Ω , from which we can finally calculate $\Delta p_V = \Omega/\pi R$.

Note that our atomic force microscopy experiments afford us quantitative access to most of the variables that appear in both the Hencky and Vella equations: membrane thickness nt , footprint radius a , and height h . This allows us to perform a rigorous comparison between the internal pressures implied by each equation. Here we assume that the Young modulus for MoS₂ is $E = 270$ GPa, as widely cited in the literature.

Surprisingly, the two equations produce quantitatively consistent results, even though the force curve approach does not explicitly use E , η , or n . By balancing $\Delta p_V = \Delta p_H$, we yield two dimensionless quantities h^3/a^3 and $a\Delta p_V/Ent$. As shown in Figure 5b, the experimental data points scaled by these two dimensionless quantities are linearly related, upholding the consistency between the Hencky and Vella equations. We also show a comparison between the absolute internal pressures computed by the two approaches. The error propagated from the Hencky technique is an order of magnitude larger than the Vella technique. In fact, we must point out that the measurement error for the Hencky technique that we present in Figure 5c is severely underestimated, because it already takes advantage of our unambiguous measurement of membrane thickness, presented in Figure 3. Previous estimates in the literature have typically used a separate Hencky formula to estimate the membrane thickness, which carries its own propagated error as we mentioned above. It also assumes E and η contribute zero measurement error. What gives our force curve technique a much smaller measurement error is the fact that it requires only the two variables R and the gradient Ω . Particularly, as one can see in Figure 5a, due to the superlative spatial resolution of AFM, the typical standard error of the gradient arising from a least-squares estimate is very small, at 0.5%.

In conclusion, our Letter demonstrates how systematic and careful atomic force microscopy allows nanoblister to be characterized accurately and unambiguously. We show three strategies to enhance the accuracy of existing estimates of mechanical properties of nanoblister. First, we unambiguously resolve nanoblisters composition by rupturing it with an AFM tip. Second, we use the profile of a ruptured nanoblisters to unambiguously infer membrane thicknesses. Third, we offer a technique to measure internal pressures of nanoblister that avoids the Hencky formulation altogether. Combining information from all three modalities, we are able to estimate the internal pressure of a nanoblisters, retrieving a value quantitatively consistent with the Hencky estimate but with a 1 order lower measurement error.

We envisage that our findings will be valuable in applications from nanodevice manufacturing to clean energy technologies. Nanoblister are especially exciting for clean energy because they exploit the superlative mechanical properties of 2D materials to contain gases such as hydrogen at standard pressure and temperatures, in stark contrast with the current use of pressurized or cryogenic storage.^{39,40} In previous work, we showed that the water-splitting technique used to create the nanoblister studied in this Letter achieves a gravimetric storage capacity of 5.3 wt %, close to an ambitious 7.5 wt %

target set by the US Department of Energy.³⁹ Ongoing efforts to optimize the efficacy of nanoblister for this and other impactful applications should be augmented by accessible, unambiguous, and accurate characterization of mechanical properties. It is our hope that the techniques presented in this Letter will aid in advancing these broader efforts.

■ ASSOCIATED CONTENT

Supporting Information

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Methods and materials (PDF)

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Author Contributions

B.H.T. and H.A. conceived the initial idea for this research. H.A. guided the work. J.Z., J.J., C.H.O., and Y.H. prepared and characterized the experimental samples. B.H.T., H.A., and K.O. carried out the experiments and analyzed the data. B.H.T. and H.A. carried out the theoretical analysis. B.H.T., N.-T.N., and H.A. wrote the manuscript.

Notes

The authors declare no competing financial interest.

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