

Mechanistic Study of Mechanical Collapse in Simulated Nanoparticle Monolayers

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ABSTRACT

2-dimensional materials formed from nanoparticles can be tailored to suit a wide range of needs, with applications that span optics, microelectronics, and catalysis. One example is thiol-ligated gold nanoparticle monolayers, which demonstrate tensile strength of magnitudes unusual for a monolayer. The nanoparticles consist of a solid gold core completely ligated with dodecanethiol chains. When placed in water and subject to uniaxial compression, the nanoparticles will self-assemble into a one-dimensional sheet. Previous experiments have used a Langmuir trough to examine the tensile strength of the sheet under such compressions, with a Wilhelmy plate used to monitor parallel and perpendicular surface pressures relative to the axis of compression. The recorded pressures are then used to calculate the strain and stress moduli of the sheet as compression continues. Of interest is the mechanism by which the monolayer collapses into a bilayer. This project uses molecular dynamics simulations to investigate the mechanism of the collapse. It was found that simulated strain/stress moduli curves match experimental ones, indicating that this model is highly relevant towards mechanistic studies. It was also proven that this system is at equilibrium, verifying key experimental assumptions. Height distributions of particles in the monolayer and newly formed bilayer are the starting point for mechanistic studies, which will soon be followed by pressure and free energy distributions in the neighborhood of local collapse. It is hoped that by understanding the mechanism of collapse, self-assembling monolayers may be eventually applied towards macroscopic self-assembling materials.

METHODS AND MATERIALS

Experimental Design

- A Langmuir trough is a rectangular array of barriers designed to cordon nanoparticles, and two opposite barriers are moveable to allow for compression
- The trough is placed in water, the nanoparticle are deposited onto the surface and the Wilhelmy plates inserted
- Uniaxial compression begins by slowly bringing together the moveable plates
- Parallel and perpendicular surface pressure and trough area are continuously recorded
- The resulting isotherm is used to calculate the strain/stress moduli, assuming equilibrium throughout the compression

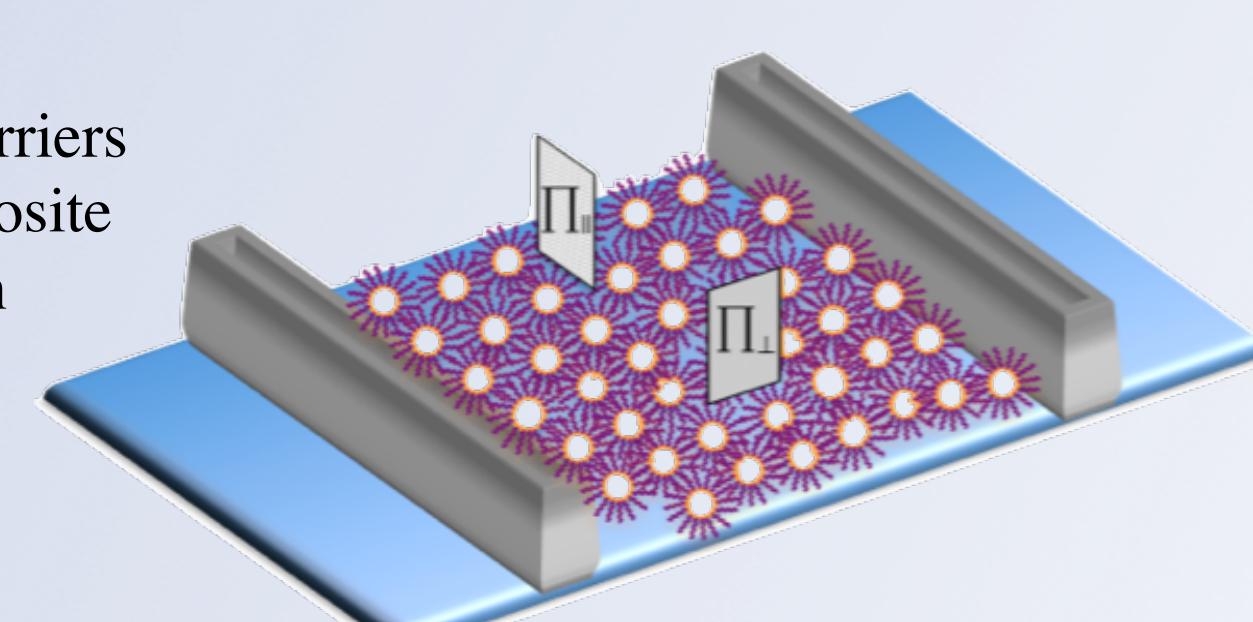


Fig. 1: A Langmuir trough setup. The Wilhelmy plates measure the parallel (Π_{\parallel}) and perpendicular (Π_{\perp}) surface pressures during uniaxial compression [3].

Simulation Design

- Molecular dynamics (MD) simulations in the canonical ensemble were written to match the experimental setup above; nanoparticles were spheres governed by the potential below
- Walls were simulated by using asymmetric harmonic potentials
- Compression rate was $5\text{cm}^2/\text{minute}$, $11 \times 7\text{ cm}$ to $1.5 \times 7\text{ cm}$, to match experiment [1]
- Potential function was designed to describe the interaction of cross-linking ligands when the nanoparticles are brought in close proximity to each other
- This system ignores the effects of other bodies and the water in the system
- Potential function U defined by algebraic repulsive term, exponential attractive term, and Gaussian correctional term, respectively, and the constants are set to represent a ligand density of 3.3 ligands/nm^3 [4]:

$$U(r) = \epsilon \left[\left(\frac{\sigma_R}{r} \right)^{64} - e^{-(r-r_A)/\alpha_A} + G e^{-(r-r_G)^2/(2\sigma_G^2)} \right]$$

The surface tensor evaluated at some point along the surface, with a box smooth-surface filtering function, is given by σ_{ij} , from which the surface pressure Π may be derived:

$$\Pi_s = \frac{-1}{4A} \sum_{\alpha} \sum_{\beta \neq \alpha} F_{\alpha\beta} \cdot (y^{\beta} - y^{\alpha})$$

Finally, for an isotherm, the shear modulus K and strain modulus G are easy to derive:

$$K = \frac{-A}{2} \left(\frac{\partial \Pi_{\parallel}}{\partial A} + \frac{\partial \Pi_{\perp}}{\partial A} \right) \quad G = \frac{-A}{2} \left(\frac{\partial \Pi_{\parallel}}{\partial A} - \frac{\partial \Pi_{\perp}}{\partial A} \right)$$

RESULTS

Qualitative Results

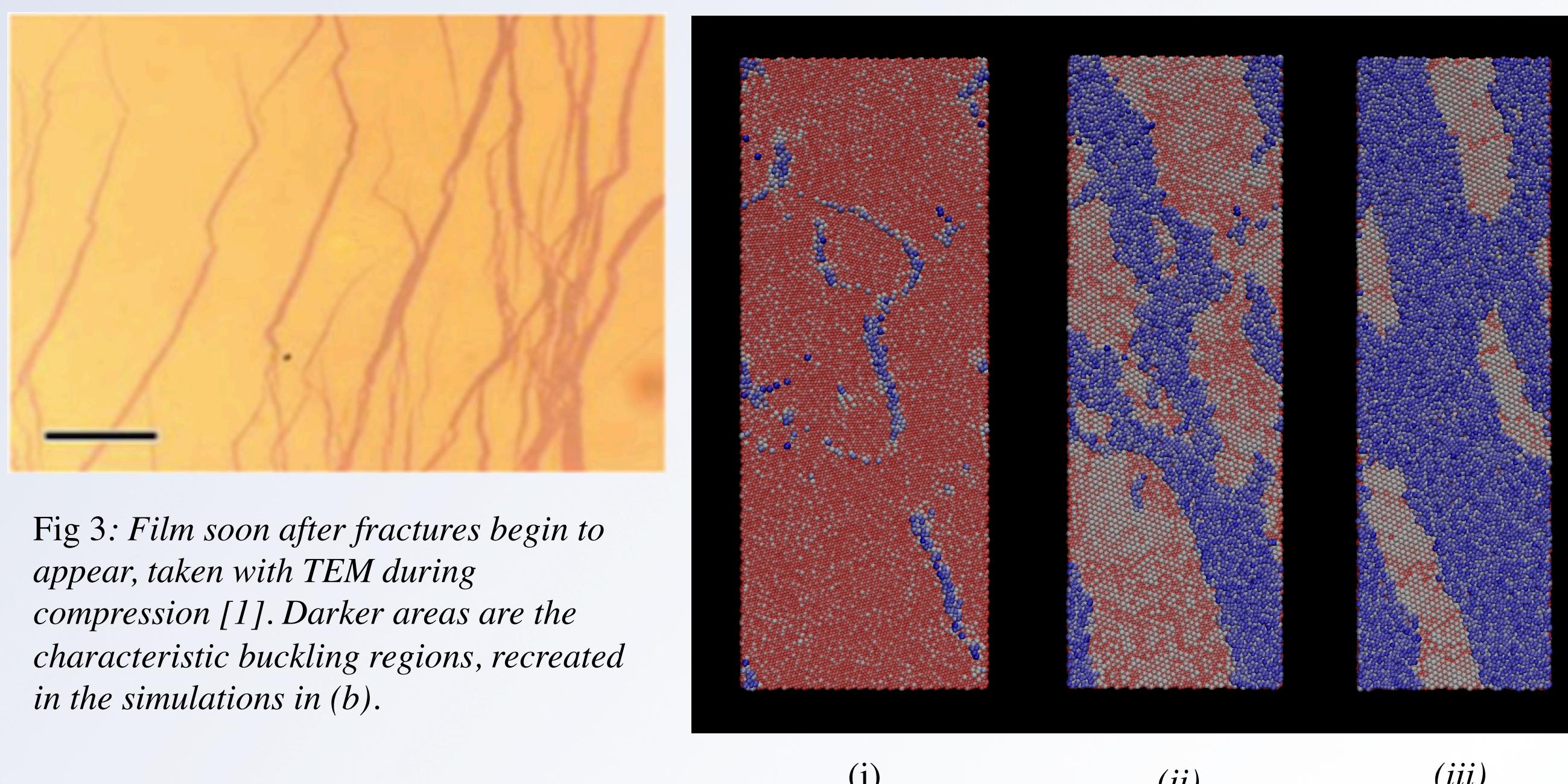


Fig. 3: Film soon after fractures begin to appear, taken with TEM during compression [1]. Darker areas are the characteristic buckling regions, recreated in the simulations in (b).

Fig. 4: Simulations show fractures very similar to those seen in experiment. Particles are colored according to their height, with red at the bottom through dark blue at the top in the bilayer. In (i), particles have initially ‘jumped’ into the bilayer at grain boundaries. The fractures grow along these initial clusters, as seen in (ii), until finally filling in, as in (iii). Also of notice is the local structures in the bottom and top layers—the bottom layer is nearly perfectly packed, whereas the top layer initially favors diffuse packing that eventually becomes a square lattice.

Isotherms and Moduli

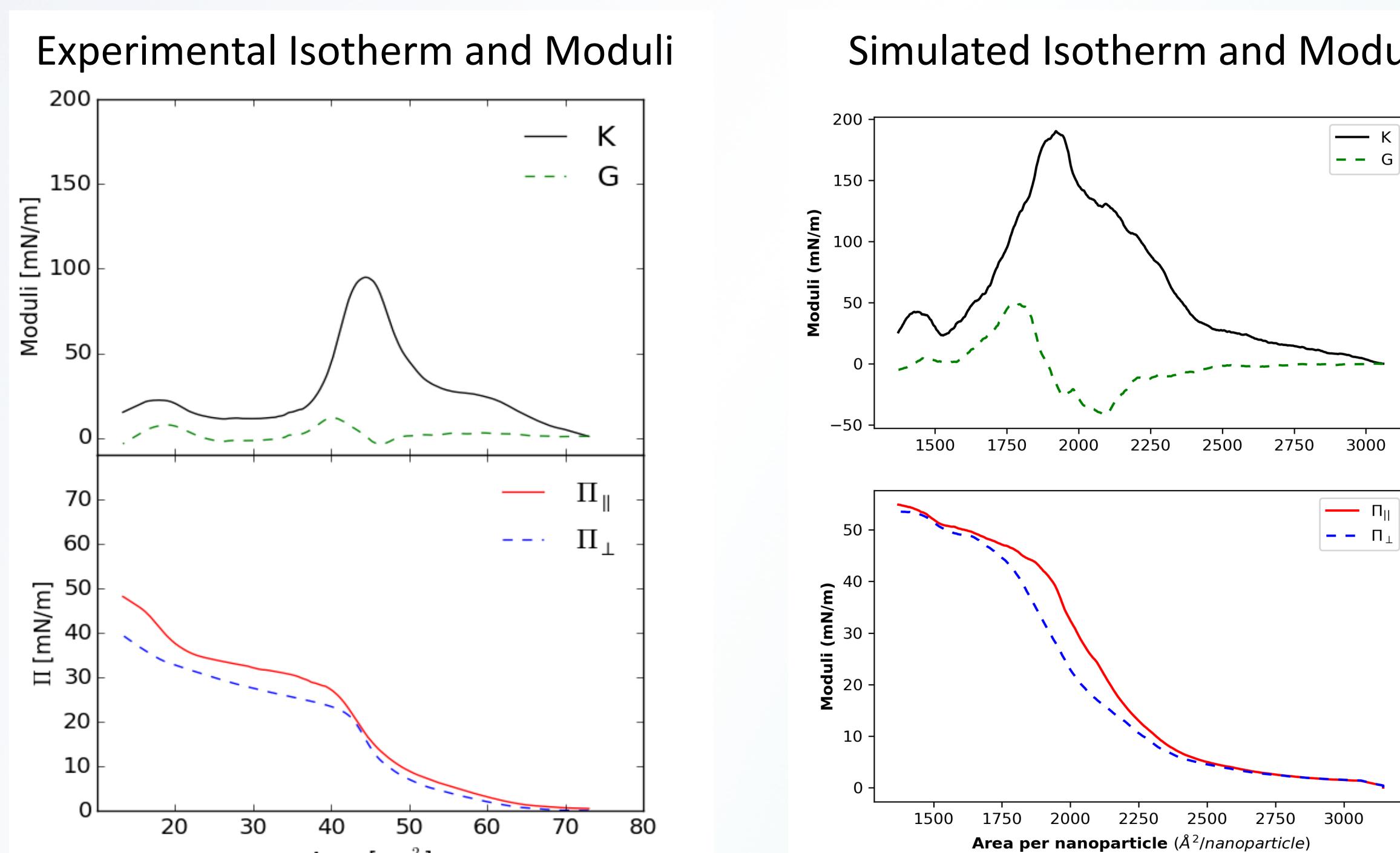


Fig. 5: An experimental isotherm (left, bottom) and moduli plot (left, top) show that initially, surface pressure climbs rather slowly (moving right to left) as the shear modulus grows. The monolayer rapidly gains surface pressure around 45 cm^2 , which corresponds to a major peak in the shear modulus, which then declines as the surface pressure grows slowly once again. This rapid transition corresponds to the collapse of the monolayer into the bilayer, when the grain boundaries with a few isolated bilayer particles grow rapidly. This activity is quite clearly reproduced in these simulations, as the same graph shapes and similar surface pressures are observed.

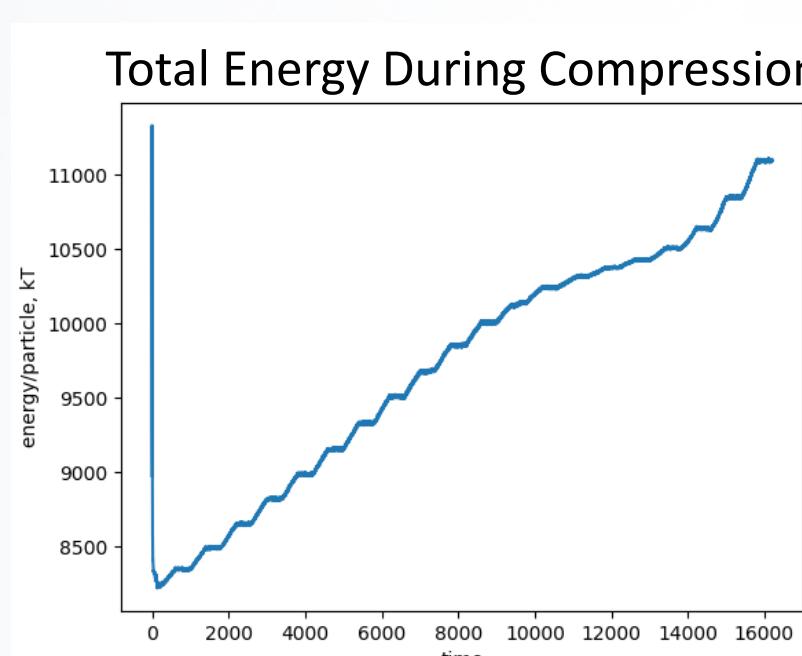
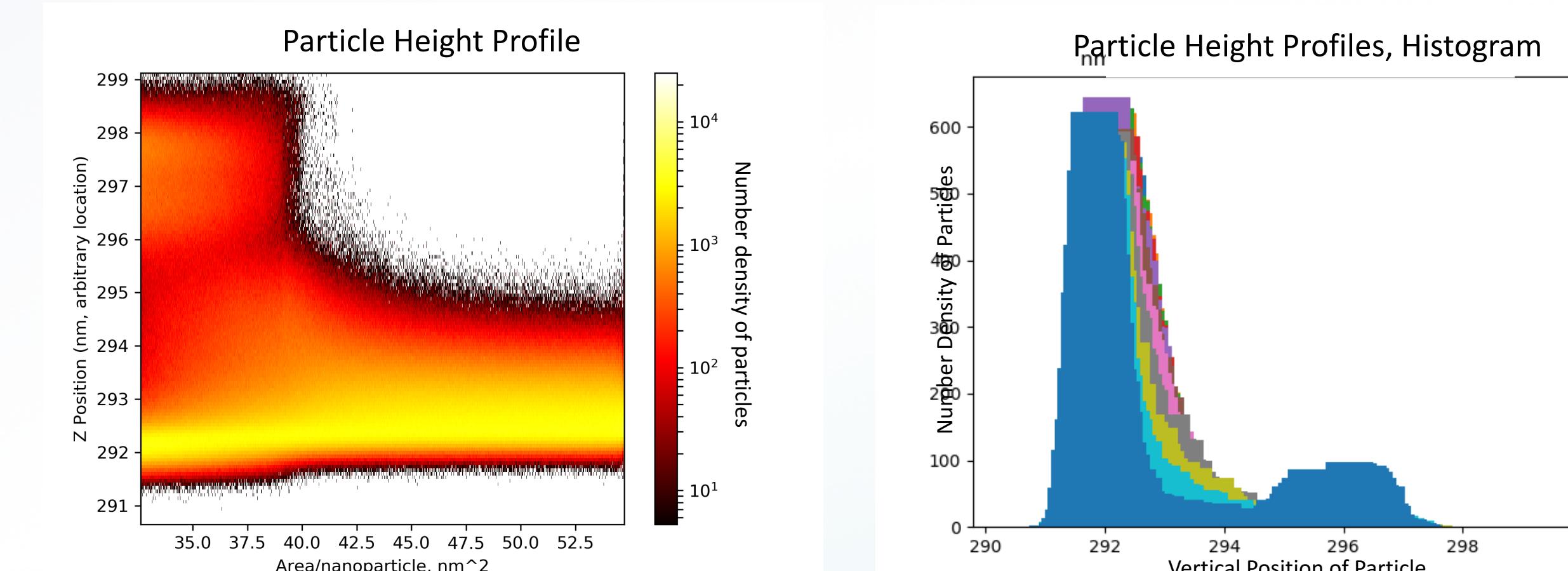


Fig. 6: Proof of equilibrium. The compression was regularly paused to see if total energy would change, but no energetic relaxation occurred (i). Deviations from perfectly straight lines during these pauses are shown in (ii)—the maximum deviation was about 1%.

RESULTS, CONTINUED

Height Distributions



- Initial mechanistic observations show that that particle height profiles are not slow changes
- On the left, each vertical ‘silver’ is a histogram for a particular particle density, whose height has been condensed into color
 - Observe that the particles are confined almost entirely to a monolayer until right around $40\text{ nm}^2/\text{particle}$, when it suddenly jumps to the bilayer
 - There is also a dark groove of no particles between the monolayer and bilayer, indicating two distinct regions rather than a ‘heap’ on top
- On the right, the histograms have been stacked into the page
 - Show that a short-lived intermediate region does exist, but when the bilayer forms, particles will transition through the intermediate but rapidly move into one region or the other

DISCUSSION

- Simulations show similar buckling patterns as experiment, and have very similar functional forms for the isotherm and moduli, indicating that this model is an accurate representation of experiment
- While the ‘area per nanoparticle’ is somewhat arbitrary due to the small simulation size, the match in surface pressure between the experiment and the model is phenomenal, and this carries over to predicting the moduli to experimentally reproducible values
- It was shown that the system is at equilibrium throughout the compression, so the isotherm match also provides strong evidence that the experimental assumption of equilibrium is valid
- Initial height studies show that the transition from a monolayer to a bilayer is preceded by a rapid intensification of surface pressure and a sharp peak in the shear modulus (but no effect on the strain modulus)

CONCLUSIONS

- The potential function used to model the interactions of the ligand-capped nanoparticles provides an excellent quantitative fit to experimental data, especially with the direction and growth of buckling fractures to well after the collapse of the monolayer into a bilayer
- Experiment this model is based is on very likely at equilibrium
- Initial results indicate that collapse of monolayer to bilayer is strongly pressure-dependent, but further research into the mechanism of both preliminary ‘jumping’ and later ‘folding’ is needed to explain how and why mechanical failure occurs

References

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Acknowledgements

This work was supported by the University of Chicago Materials Research Science and Engineering Center, NSF-DMR-1420709. B.L. acknowledges the support from ChemMatCARS that is funded by the NSF (CHE-1834750).