Elastic nanomembrane metrology at fluid–fluid interfaces using axisymmetric drop shape analysis with anisotropic surface tensions: deviations from Young–Laplace equation†

James K. Ferri,a* Paulo A. L. Fernandes,†b J. Tyler McRuiza and Filippo Gambinossia

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Fluid–fluid interfaces are an attractive template for engineering nanomembranes via self-assembly. Although an increasing number of investigations of the local (~10⁻³ m²) surface mechanics of a variety of materials, detailed studies of mechanical behavior and the constitutive parameters over larger areas (>10⁻⁶ m²) are relatively scarce. This is because of the limitations of quantitative experimental techniques due to the asymmetry of the length scales involved. Here, we discuss fabrication and characterization of a polysaccharide and polyamino acid-based nanomembrane having a thickness of approximately 200 nm and surface area of 25 × 10⁻⁶ m² and present mechanical data for hyaluronic acid–poly-L-lysine nanomembranes using a modified pendant drop as a test frame. Covalent cross-linking of these molecules at fluid–fluid interfaces leads to the formation of supramolecular networks which confer properties such as mechanical rigidity that are outside of the description provided by equilibrium surface thermodynamics. A theoretical framework for data interpretation of purely elasticity interface systems is provided, and experimental signatures of anisotropic tension distributions on axisymmetric drop and bubble shapes are identified. By taking advantage of the mechanical transparency of the fluid–fluid interface, this method provides a means of accessing mechanical properties of ultrathin materials independent of artifacts, such as adhesion, introduced by a solid substrate.

Introduction

The mechanical behavior of elastic surface networks formed by adsorption and interfacial complexation has received increased interest in recent years, partly because templating at fluid–fluid boundaries has become a widely used method for the fabrication of nanostructured membranes.1 Progress in understanding mechanical performance of elastic nanomembranes fabricated at mesoscopic sizes has been limited due to the lack of suitable instrumentation and methods.2 Therefore, the elaboration of both experimental methods and theoretical frameworks for their interpretation are important in advancing both the science and technology of mesoscopic materials transversely constrained to molecular and supramolecular dimensions. Fundamental interest also exists in modeling the mechanics of interfaces resulting from adsorption and complexation of surfactants, macromolecules, and nanoparticles, and composites thereof.3

In the Gibbs convention, the interface between two immiscible fluids can be described in two dimensions, therefore it cannot support bending moments. The principal curvatures, \(K_1\) and \(K_2\), in the two surface directions define the shape of the interface, and the forces in the interface can be expressed as a surface stress tensor with units of force per unit length. For a pure fluid, the in-plane stresses can be expressed in terms of a single isotropic tension \(\gamma\), the thermodynamic surface tension, which is related to the attractive intermolecular interactions in the bulk phase and the loss of coordination for molecules at the interface. The conditions of mechanical equilibrium can be used to derive the classical Young–Laplace relationship, shown in eqn (1). Eqn (1) describes the shape of a fluid interface by relating the isotropic interfacial tension, the curvature of the interface, and the pressure jump \(\Delta p\) across it:

\[
\gamma(K_1 + K_2) = \Delta p
\]

According to the Gibbs adsorption equation,4 when amphiphilic molecules adsorb at a fluid interface, the surface excess concentration, \(I\), increases and the thermodynamic surface tension, \(\gamma(I)\), decreases from the pure fluid surface tension, \(\gamma_0\). However, in the absence of deformation, the tension remains isotropic. During stretching, interfacial stresses can develop in
response to the applied strain, but when surface molecules do not interact, as in an ideal surface gas, the stress remains isotropic.

Interfacial dilational rheology is a commonly used method to assess the interactions between surface molecules. In these experiments, the interfacial stress resulting from the deformation of the surface of a pendant drop or bubble due to expansion or contraction is measured. Anisotropic surface stresses can result during inflation when surface molecules interact to form an elastic interfacial network. Here, we describe and analyze a mechanical framework for the inflation of a pendant drop or bubble as well as the associated interfacial strains and tensions for fluid interfaces that can support anisotropic stresses.

Purely elastic interfaces are specifically addressed, although extension to viscoelasticity is straightforward. Purely dissipative interfaces can be described by eqn (1).

To demonstrate these effects experimentally, we compare the mechanical behavior of polyelectrolyte multilayers fabricated by electrostatic self-assembly of hyaluronic acid (HA) and poly-L-lysine (HA) using layer-by-layer adsorption with and without interlayer covalent cross-linking at the air–water interface using quasi-static inflation of a pendant drop.

In the absence of cross-linking, the inflation results in axisymmetric drop shapes adequately described by a single isotropic surface stress, i.e. the Young–Laplace equation. For this system, we consider the interfacial stresses in response to inflation that exceed the limits imposed by Gibbs surface thermodynamics. Additionally, the shapes during inflation deviate systematically and measurably from the profiles predicted by the Young–Laplace equation. This suggests that there are signatures of elastic network formation in experimental drop shape data when analyzed with the Young–Laplace equation.

Experimental

The experimental setup is a coaxial capillary pendant drop (CCPD) tensiometer (PATID, Sinterface Technologies, Germany); a schematic is shown in Fig. 1a. In short, a silhouette of a pendant drop formed at the tip of a capillary is cast onto a CCD camera and digitized. A specially constructed capillary consisting of a concentric geometry made of glass microtubing and polyetheretherketone is used for drop formation. This geometry allows a drop of aqueous solution to be formed at the capillary tip, and the subphase to be exchanged by injection (Microinjector 2) and withdrawal (Microinjector 1) of liquid from the droplet interior at a matched volumetric flow rate (\( R_F \approx 3.0 \times 10^{-10} \text{ m}^3 \text{ s}^{-1} \)). During the exchange, interfacial area, \( A \approx 25 \times 10^{-6} \text{ m}^2 \) of the drop is maintained constant by feedback control using Microinjector 1. The digital images of the drop are recorded over time and fit to the Young–Laplace equation to accurately \( \pm 0.1 \text{ mN m}^{-1} \) determine surface tension.

Nanomembrane fabrication

A schematic of the technique for the synthesis of an ultrathin free-standing nanocomposite is shown in Fig. 1b. A dimyristoylphosphatidyl glycerol (DMPG) anionic lipid monolayer is deposited onto a pendant drop of aqueous buffer solution and compressed to achieve a specified surface density of template molecules. The subphase of the drop is then exchanged maintaining constant surface area with a subphase containing poly-L-lysine (PLL). Alternate cycles of PLL and hyaluronic acid sodium salt (HA) with ultrapure water with a 0.15 M sodium chloride (NaCl) ionic buffer result in a free-standing polymeric nanocomposites having a thickness defined by the number of adsorption layers. All polyelectrolytes and other reagents were dissolved in 0.15 M NaCl (pH 6–6.5) at a concentration of 1 mg mL\(^{-1}\) unless otherwise noted. The DMPG spreading solution was prepared at a concentration of approximately 0.35 mg mL\(^{-1}\) using ultrapure (99.9%) chloroform and methanol, approximately (3 : 1 v/v) from J. T. Baker and delivered via a microsyringe (Hamilton, US) to the air–water interface of the pendant drop. DMPG, PLL (\( M_W \sim 60 \text{ kDa} \)), HA (\( M_W \sim 400 \text{ kDa} \)), and NaCl were purchased from Sigma-Aldrich and used as received. The water used in all experiments was purified in a Milli-Q purification system and had a resistivity of approximately 18.2 M\( \Omega \) cm\(^{-1}\).

Multilayers of (HA/PLL) can be cross-linked via the carboxylic acid–amide inter-layer functionality. In short,
N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) can be used to activate the carboxyl moiety on HA. This complex is converted to an active ester via hydroxy-2,5-dioxopyrrolidin-3-sulfonic acid sodium salt (sulfo-NHS). The active ester reacts with primary amine bonds on the PLL to form an amide linkage. EDC and sulfo-NHS were also purchased from Sigma-Aldrich. Cross-linking was carried out by exchanging a 0.15 M NaCl solution at (pH ~ 5.2) containing 200 mM EDC and 50 mM sulfo-NHS and holding at constant interfacial area (\(A = 25 \times 10^{-6} \text{ m}^2\)) for 12 hours.

Mechanical metrology

Mechanical characterization of freestanding nanomembranes is accomplished via non-contact deformation (25 \(\times\) \(10^{-6}\) m\(^2\) < \(A < 40 \times 10^{-6}\) m\(^2\)) of the nanomembrane by hydrostatic inflation.\(^{10}\) First, a nanomembrane is synthesized according to the pendant drop method outlined in the previous section. Then, the interfacial area, \(A\), of the pendant drop is increased by injection of liquid into the subphase of the pendant drop. This process is monitored by feedback control using in situ digitization of the drop to numerically calculate its surface area and hence control size in real time. By measuring the shape of the deformed drop surface it is possible to infer the elastic properties of the membrane by the inverse method described above. A ramp strain was used in all experiments with a rate of 1.5 \(\times\) \(10^{-3}\) m\(^2\) s\(^{-1}\).

Theory

Consider the shape of a pendant drop, covered by a purely elastic network of surface molecules. This surface can be treated as an interface having an isotropic thermodynamic surface tension \(\gamma\) and elastic membrane tensions \(T_1\) and \(T_2\) in the two surfaces, presenting the possibility of an anisotropic stress distribution. Cylindrical coordinates \((r_0, \phi_0, z_0)\) characterize a point on the membrane in the undistorted state, or the surface coordinates \((\xi_0, \phi_0); \) as shown in Fig. 2.

Elastic membrane tensions result from deformation; therefore in the absence of deformation \(T_1 = T_2 = 0\). In this case, the Young–Laplace equation describes the shape of the undeformed interface in terms of the equilibrium thermodynamic surface tension \(\gamma\). Extensive literature documents the solution of eqn (1), see Appendix A for a brief overview.

When subjected to an internal inflationary load such as hydrostatic pressure, this deforms to a shape described by the coordinates \((r, \phi, z)\) or \((\xi, \phi)\). The expectation of rotational symmetry implies \(\phi_0 = \phi\), therefore motion of a point during inflation can be expressed as \(r(\xi_0)\) and \(z(\xi_0); \) knowledge of these functions specifies the shape of the membrane in the deformed state.

The deformation of the interface is characterized by the eigenvalues of the strain tensor; the principal stretches in the directions of the surface coordinate lines associated with the surface strain are

\[
\lambda_1 = \frac{\partial \xi}{\partial \xi_0} = \sqrt{r^2 + z^2} \quad (2a)
\]

\[
\lambda_2 = \frac{r}{r_0} \quad (2b)
\]

where the subscripts 1 and 2 denote the meridional (\(\xi\)) and azimuthal (\(\phi\)) surface directions, respectively. The prime denotes differentiation with respect to the undeformed arc length \(\xi_0\).

As the dilation of the interface proceeds, surface stresses or tensions develop in response to its stretching. For isotropic surface materials, the stretches and stresses are collinear. The physical components for the interfacial stress tensor \(S_{11} = S_1\) describing the shape of the deformed interface are assumed to be of the form

\[
S_1 = \gamma(T) + T_1(\lambda_1, \lambda_2) \quad (3)
\]

The surface stress in the orthogonal surface direction 2 is obtained by exchanging indices 1 and 2. Eqn (3) states that the total surface stress \(S\) is the sum of the thermodynamic surface tension \(\gamma\) and the membrane stress \(T\) resulting from deformation, an approach used previously to separate surface tension effects from membrane contributions in Pickering emulsion droplet deformation.\(^{11}\) The simplest form of membrane tensions assumes that the surface stress is linear in the surface deformation; this is the surface equivalent of Hooke’s law. Linear elasticity is typically restricted to small deformations. In this case, the membrane tension is

\[
T_1 = \frac{G_e}{1 - v_e} \left[ \lambda_1^2 - 1 + v_e (\lambda_3^2 + 1) \right] \quad (4)
\]

where \(G_e\) (usually expressed in mN m\(^{-1}\)) and \(v_e\) (a dimensionless quantity \(-1 < v_e < 1\)) are the surface shear modulus and the surface Poisson ratio of the membrane. For an incompressible Hookean surface \(v_e = 1\). To describe large deformation behavior, non-linear constitutive laws are usually required. The impact of surface constitutive behavior on membrane stretching is discussed elsewhere.\(^{12}\)

The equations of equilibrium are the result of the balance of linear momentum and the geometric relationships. The local force balance in the membrane requires that the divergence of the stress in the membrane equals the jump of pressure across it. The force balance has two tangential components and one normal component. The normal and the tangential (\(\xi\)) components of the force balance are

\[
\frac{\partial S_1}{\partial r} - \frac{1}{r} (S_1 - S_2) = 0 \quad (5a)
\]
where the principal curvatures can be expressed as

\[ K_1 = \frac{\theta'}{\lambda_1}, \quad K_2 = \frac{\sin \theta}{r} \]  

The tangential (\( \phi \)) component is identically satisfied by axisymmetry.

The normal pressure jump [\( p \)] is given by the hydrostatic pressure, i.e. \[ [p] = [p]_0 - \Delta \rho g z. \] Eqn (5) and (6) together with the geometric relations

\[ r' = \lambda_1 \cos \theta \]  

\[ z' = \lambda_1 \sin \theta \]

The deformed shape is calculated by the integration of eqn (5)–(7) for a specified inflation. The inflation \( \alpha \) is defined as

\[ \alpha = \frac{A - A_0}{A_0} \]  

where \( A_0 \) is the reference area, and the deformed area \( A \) is

\[ A = \int_0^\frac{\pi}{2} 2\pi r\lambda_1 d\xi_0 \]  

The effect of the surface shear modulus on the inflated shape is shown in Fig. 3. The axes of the deformed coordinates \( (r, \xi) \) are scaled using the radius of the capillary \( \alpha = r_0(\xi_0 = s_0) \) from the undeformed shape. Results show that the deformed shape is sensitive to the surface shear modulus; as the surface shear modulus increases, the deformed profile tends toward a spherical shape. This can be described by considering the competition between gravitational forces and surface elastic membrane tensions during inflation. Gravity extends the drop from the spherical shape, and the surface elastic membrane tensions act to oppose elongation. The ratio of gravitational to surface tension forces is described by the Bond number, \( Bo = \Delta \rho g a^2 / \sigma \), where the surface tension force, \( \sigma \), is represented using the isotropic surface stress:

\[ \sigma = \frac{1}{2} (S_1 + S_2) \]  

Limiting cases: isotropic interfacial tension

Using the equations developed in the previous section, the shape of a pendant drop governed by isotropic interfacial tension alone can be recovered for two different cases. The first case is that of zero deformation where the principal stretches \( \lambda_1 = \lambda_2 = 1 \). The second case is that of zero membrane elasticity where \( G_\theta = 0 \). Additionally, in microgravity, the internal pressure is constant, and an isotropic tension is capable of describing the shape, because \( \lambda_1 = \lambda_2 = \lambda \) corresponds to a spherically symmetric inflation. For isotropic materials, when the stretches are equal, the stresses are equal.

In the first case, eqn (7) show that the membrane stresses are identically zero when \( \lambda_1 = \lambda_2 = 1 \). Eqn (3) becomes \( S_1 = S_2 = \gamma(\Gamma) \), and eqn (5a) is identically satisfied. Eqn (5b) becomes eqn (1). There is only one inflation from eqn (8) that satisfies this criteria; \( \alpha = 0 \). The shapes calculated by eqn (1), the Young–Laplace equation, and eqn (5), the anisotropic surface stress equations are identical; see ESI.† The same occurs for all deformations when \( G_\theta = 0 \).

Linear elastic nanomembranes at axisymmetric fluid–fluid interfaces: effect of surface shear modulus on drop shape, surface deformation, and surface stresses

What are the differences between the inflation of a pendant drop described only by isotropic surface tension and that of a surface having an anisotropic distribution of surface tensions caused by the presence of an elastic membrane? For simplicity, all calculations utilize the assumption of linear elasticity, as in eqn (4), to describe surface constitutive behavior. Extension to non-linear elastic behavior of membrane stretches is straightforward.

An isotropic thermodynamic tension, \( \gamma(\Gamma) \), of 50 mN m\(^{-1}\), the approximate interfacial tension of a protein monolayer at the air–water interface, is used in the calculations that appear in eqn (3). This corresponds to the experimentally measured equilibrium surface tension of pendant drop after the synthesis of the DMPG–(HA–PLL)\(_4\) nanomembrane and before inflation.

Variation in the surface shear modulus reflect changes in the thermophysical properties of the nanomembrane such as the strength (electrostatic vs. covalent) or number density (cross-link density) of intermolecular interactions in the surface.

The effect of the surface shear modulus on the inflated shape is shown in Fig. 3. The axes of the deformed coordinates \( (r, \xi) \) are scaled using the radius of the capillary \( \alpha = r_0(\xi_0 = s_0) \) from the undeformed shape. Results show that the deformed shape is sensitive to the surface shear modulus; as the surface shear modulus increases, the deformed profile tends toward a spherical shape. This can be described by considering the competition between gravitational forces and surface elastic membrane tensions during inflation. Gravity extends the drop from the spherical shape, and the surface elastic membrane tensions act to oppose elongation. The ratio of gravitational to surface tension forces is described by the Bond number, \( Bo = \Delta \rho g a^2 / \sigma \), where the surface tension force, \( \sigma \), is represented using the isotropic surface stress:

\[ \sigma = \frac{1}{2} (S_1 + S_2) \]  

When the Bond number is zero, the deformed shape is spherical. This occurs under microgravity conditions, where \( g = 0 \), for isodense fluids, where \( \Delta \rho = 0 \), for small experimental geometries where the radius of curvature is small, or \( \alpha = 0 \), and...
lastly for deformations which result in sufficiently large surface stresses, either because of large surface shear moduli or large deformation. This last case is the most important. Regardless of $G_s$, as inflation increases, the Bond number decreases asymptotically toward zero. For the same inflation with increasing surface shear modulus, the rate of approach of Bo towards to zero increases. This suggests that shape differences between surfaces of different moduli decrease as inflation proceeds. This is because the inflation of any elastic surface will eventually tend toward the spherical shape, a phenomenon previously discussed by Müller and Strehlow.13

The meridional stretching ($\lambda_1$) is maximum at the drop apex and that as the surface shear modulus increases, non-monotonic behavior develops in ($\lambda_2$). However, in all cases, the magnitude of the stretches is similar. This is because the undeformed Young–Laplace shape is similar to a sphere ($\lambda_1 \approx \lambda_2$). And for a specified inflation, the product of the stretches is constrained by

$$\alpha = \lambda_1 \lambda_2 - 1 \quad (11)$$

It is then expected that the magnitude of the stretches be similar regardless of $G_s$. Details can be found in ESI↑

Fig. 4 shows the total surface tension resultants ($S_1, S_2$) for the deformed configurations under the same conditions as in Fig. 3. In Fig. 4, the total undeformed arc length, $s_0$, scales the undeformed arc length coordinate $\xi_0$.

The differences in the principal tensions $S_1$ and $S_2$ as a function of $G_s$ are more dramatic than between the principle stretches, because the magnitude of the stress scales more directly with the magnitude of the surface shear modulus. However, it should be noted that although there is an order-of-magnitude increase in $G_s$ between Fig. 4a and d, there is only a roughly five-fold increase in the maximum value of the total surface stress $S_1$. It should also be noted that the surface stress is maximum at the contact line with the capillary $\xi_0 = 0$; this is intuitive because the membrane is supporting the weight of the drop at this point. This suggests an inherent vulnerability to membrane failure at the boundary.

**Shape differences between surfaces with anisotropic stresses and the Young–Laplace equation**

As discussed in the previous section, the inflation of any purely elastic surface will eventually tend toward the spherical shape. Therefore, it is expected that as inflation increases the shape of a surface described by eqn (3)-(7) will deviate both systematically and increasingly from that of a surface described by the Young–Laplace equation. The important question is whether or not these differences are experimentally observable.

To address this question, the shape of a drop was calculated under the assumption of anisotropic stress distribution. Then, the Young–Laplace equation was fit to this shape using an isotropic surface stress, $\sigma$ as the sole fitting parameter. The result graphs are shown in Fig. 5a.

A systematic deviation between the two shapes can be observed. The deviation can be quantified in terms of the difference between the radii of the two shapes at the same value of the axial coordinate $z$. Hereafter, this is referred to as the deviation from the Young–Laplace equation, $\delta(z)$. As previously stated, $\delta$ is expected to increase with increasing inflation, $\alpha$, and

![Fig. 3](image1)

**Fig. 3** Effect of surface shear modulus on deformed configuration; $G_s = (a) 50$, (b) 100, (c) 200, and (d) 500 mN m$^{-1}$; $\nu_s = 0$; for all calculations $\alpha = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5. $R_0 = 1320$ m$^{-1}$, $\Delta \rho = 997$ kg m$^{-3}$, $\gamma(T) = 50$ mN m$^{-1}$.

![Fig. 4](image2)

**Fig. 4** Effect of surface shear modulus on principal stresses $S_1$ (–). $S_2$ (––); $G_s = (a) 50$, (b) 100, (c) 200, and (d) 500 mN m$^{-1}$; $\nu_s = 0$; for all calculations $\alpha = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5. $R_0 = 1320$ m$^{-1}$, $\Delta \rho = 997$ kg m$^{-3}$, $\gamma(T) = 50$ mN m$^{-1}$. 

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increasing surface shear modulus, \( G_s \). This is due to the fact that all inflated profiles tend toward the spherical shape. Fig. 5b and c shows the deviation from Young–Laplace behavior for the anisotropic shapes as a function of inflation for surface shear modulus, \( G_s = 50 \text{ mN m}^{-1} \) and 500 mN m\(^{-1}\), respectively. As expected, the deviation \( \delta \) increases with increasing inflation and surface elasticity. It should be noted that \( \delta \) can be used to provide a signature of elastic network formation without the integration of eqn (3)-(7); analysis of drop shape data for surfaces with elastic behavior using the Young–Laplace equation should yield \( \delta(z) \) as seen in Fig. 5b and c. This suggests that the examination of the Young–Laplace error profile that results from fitting experimentally measured drop shapes in the method described above can yield important clues about the nature of the surface stress distribution. Insight is therefore provided into the types of intermolecular surface interactions governing mechanical response.

Fig. 5d shows the summation of \( \Delta \) for a given drop shape as a function of inflation for different surface shear moduli and surface Poisson ratio. This confirms that \( \Delta \) values, which results from using the Young–Laplace equation to describe an anisotropic surface, increases with increasing inflation and surface shear modulus. The error also increases with increasing \( \nu_s \); see ESL†. Although these errors are small in magnitude, they are systematic and more importantly measurable, demonstrating an inherent deviation between the shapes calculated using the Young–Laplace equation and those calculated using the equations capturing anisotropic surface tension distributions.

**Polysaccharide–polyamino acid nanomembranes and experimental measurement of anisotropic surface tensions**

Both PLL and HA are weak polyelectrolytes having a degree of dissociation that is a function of pH and ionic strength leading to film growth that is exponential in the number of layers. The growth pattern for (HA/PLL)\(_n\) films was studied previously.\(^{16}\)

Differences in mechanical properties of weak and strong polyelectrolyte nanomembranes are obvious. Isotropic surface stress \( \sigma \) as measured by axisymmetric drop shape analysis is plotted versus drop inflation \( \nu \) for weak polyelectrolyte nanomembrane DMPG–(HA–PLL)\(_2\) in the native and cross-linked state. Although the degree of cross-linking was not quantitatively assessed, exposure of the nanomembrane to serial cross-linking conditions resulted in an increase of the elastic modulus suggesting the initial reaction was not run to completion. Data presented here are after one cross-linking cycle. Regardless, the mechanical behavior of the native assembly is substantially different from the cross-linked material. It shows plastic deformation under relatively small inflation (see Fig. 6a), negligible and random deviation \( \delta(z) \) for each drop profile (Fig. 6b), and a small \( \Delta \) over a range of inflations (Fig. 6d).

Fig. 6a compares the mechanical response of DMPG–(HA/PLL)\(_2\) with and without cross-linking. Consider that if the isotropic surface stress is a sole function of the surface excess concentration, i.e. \( \gamma(T) \), the surface stress has an upper bound of the surface tension of the pure solvent subphase \( \gamma_0 \) – in this case approximately 72.4 mN m\(^{-1}\), the surface tension of the air–water interface. During inflation, the measured isotropic tension of the nanomembrane exceeds the limit for a Gibbs surface layer. This suggests the presence of elastic membrane tensions arising from inflation. It can also be noted that the cross-linked nanomembrane displays elastic behavior over a significantly wider range of inflation and also exhibits fracture behavior. Both nanomembranes have a thickness of approximate 200 nm.

The surface shear modulus of the native assembly is approximately 30 mN m\(^{-1}\), which translates to a bulk elastic modulus of 150 kPa. The cross-linked nanomembrane has a surface shear modulus of approximately 120 mN m\(^{-1}\), which corresponds to a bulk elastic modulus of 600 kPa. Both of these are in reasonable agreement with the previous measurement of Richert, \textit{et al.} \(^{15}\)

Fig. 6b and c compare the error profile, \( \delta(z) \), with respect to the fitted Young–Laplace equation, which assumes the drop is isotropic. There is good qualitative agreement between the error distributions predicted using the surface shear modulus as measured in Fig. 6a. Additional, there is also reasonable agreement between theory and experiment for the increase in the sum of the error \( \Delta \) for both native and cross-linked nanomembranes using the theoretical prediction.

**Conclusions**

Therefore, there is a difference in the applicability between eqn (4), (8)–(11) and eqn (2) and (3) regarding the illustration of the
shape and state of stress of the interface. This occurrence is not observed for the difference between solids and liquids, but rather for the capacity of the interface to support a non-zero deviatoric stress, \( \sigma' = S_1 - S_2 \).

This framework enables elucidating the nature of the error arising from using only the Young–Laplace equation to describe surface stresses in elastic interfacial systems and develops simplified metrics to extract information regarding surface shear modulus from experimental data. In forthcoming work, we report structure–property studies of material processing conditions on ultrathin composite systems in elastic and viscoelastic synthetic and biological systems.

Appendix A: numerical solution of Young–Laplace equation

Eqn (1) can be rearranged using the relations

\[
\theta' = \left( \frac{2}{R_0} - \frac{\Delta \rho g z}{\gamma} - \frac{\sin \theta}{r_0} \right) \tag{A.1}
\]

\[
r' = \cos \theta \tag{A.2}
\]

\[
z' = \sin \theta \tag{A.3}
\]

\[
A_0 = \int_{\xi_0}^{2\pi r_0} d\xi_0 \tag{A.4}
\]

Integration of eqn (A.1)–(A.4) give the axisymmetric drop shape governed by an isotropic tension. Here it is used for comparison to the shapes governed by anisotropic stress distributions as well as for calculation of the reference configuration \( r_0(\xi_0) \).

Appendix B: numerical solution of drop shape for anisotropic surface tension distributions

Eqn (5) can be recast using the relations

\[
f_1 = \frac{\partial S_1}{\partial \lambda_1} \tag{B.1}
\]

\[
f_2 = \frac{\partial S_2}{\partial \lambda_2} \tag{B.2}
\]

\[
f_3 = S_2 - S_1 \tag{B.3}
\]

\[
\lambda_2' = \frac{r'}{r_0} - \frac{r r_0'}{r_0^2} \tag{B.4}
\]

The solution procedure is as follows: (1) a guess is made for \( \lambda_1(0) \), (2) eqn (8) and (9) are solved, and the pressure at the apex \( \rho_{10} \) is adjusted iteratively to satisfy the condition \( \lambda_2(\xi_0) = 1 \), and (3) \( \lambda_1(0) \) is adjusted iteratively to satisfy a specified inflation. It should be noted that at \( \xi_0 = 0 \), eqn (6) are ill-defined and can be replaced by

\[
\lambda_1(\xi_0 = 0) = 0 \tag{B.7}
\]

\[
\theta'(\xi_0 = 0) = \frac{\rho_{10}}{2R_0} \tag{B.8}
\]

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