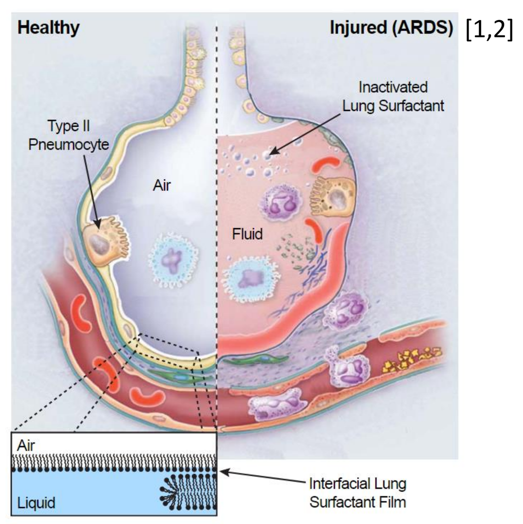
Decoupling shear and dilatational viscoelastic behaviors for complex fluid interfaces

Summer Tein[1], **Chuck Majkrzak**[2], **Brian Maranville**[2], **Jan Vermant**[3], **Norman J. Wagner**[1]

[1] Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716
[2] National Institute of Standards and Technology, Gaithersburg, Maryland, USA, 20899
[3] Department of Materials, ETH Zurich

1. Importance of Interfaces



- Lung surfactants (LS) lower pulmonary compliance to ease the work of breathing.
- ARDS and NRDS (Acute/Neonatal Respiratory Distress Syndrome) are diseases caused by lack of LS thin film stability.

- Emulsion stability can be enhanced by addition of particles/surfactants, which resist shrinkage and growth of the bubbles

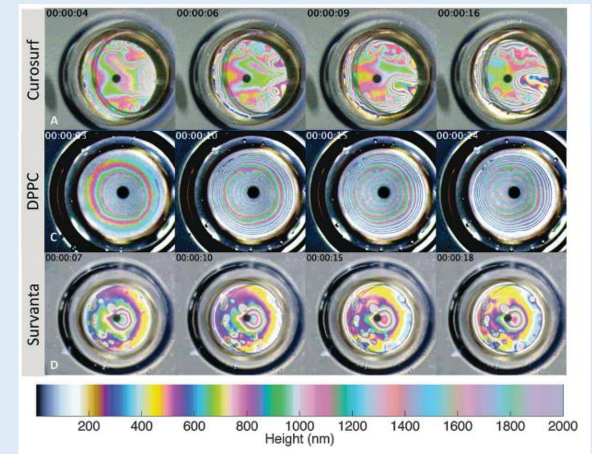
Understanding the link between the structural properties of complex fluid interfaces and their rheological mechanisms can help aid the engineering design of new synthetic materials with optimal mechanical and structural properties.

[1] Shieh, I. C. **2012.** ProQuest Dissertations & Theses A&I. (1112251417).
modified from [2] Ware, L. B., & Matthay, M. A. N. Engl. J. Med **2005**, 353(26), 2788-2796.

2. Lung Surfactants: Case Study of Interfacial Complexity

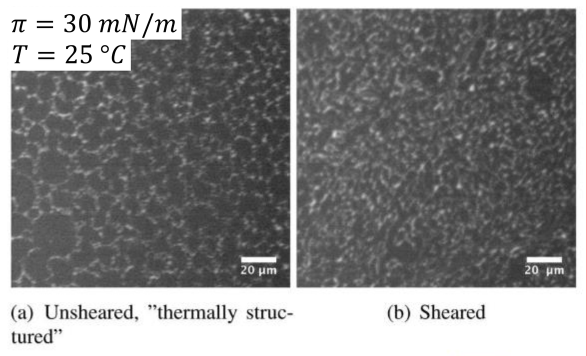
Lung surfactants and their mechanism show discrepancies in literature
We hypothesize these issues stem from chaotic processing of the interface

Drainage Interferometry[1]



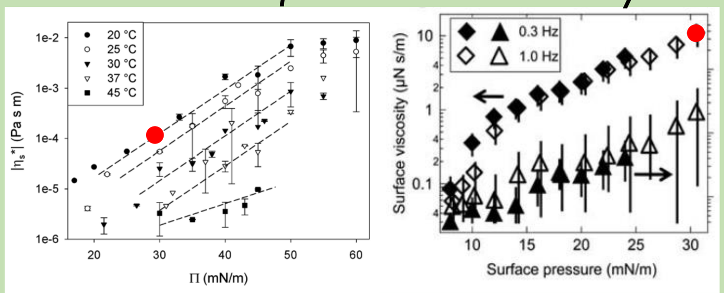
Clinical surfactants (Survanta and Curosurf) strongly differ in their interfacial viscosities and their spreading/drainage abilities.

DPPC Fluorescent Microscopy[2]

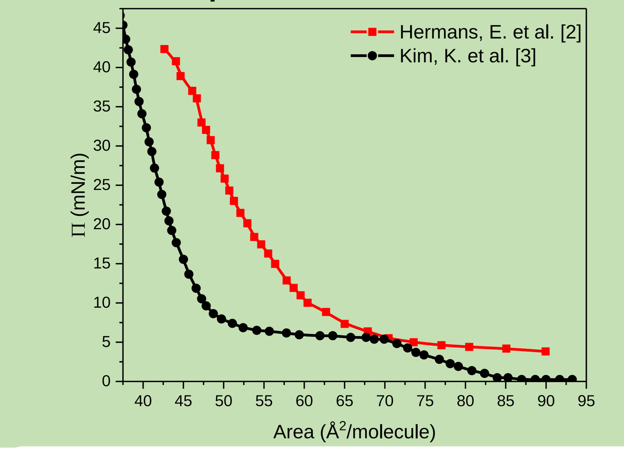


Shearing the interface can cause structural rearrangement

DPPC Interfacial Shear Viscosity[2,3]



DPPC Surface Pressure Isotherms[2,3]



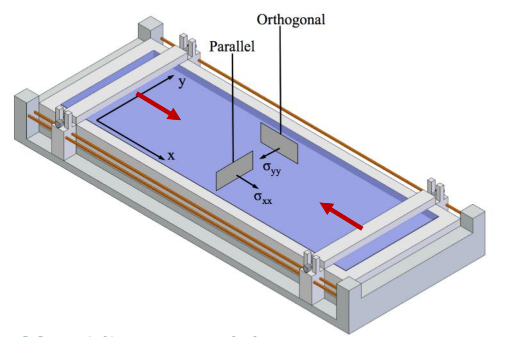
Both shear and dilatational viscosities play a role in lung surfactant stability and spreading, but rheological mechanism is still widely debated in literature.

[1] Hermans, E. et al. *Soft matter* **2015**, *11*(41), 8048-8057. [2] Hermans, E. et al. *Soft Matter* **2014**, *10*, 175–186. [3] Kim, K. et al., T. M. Soft Matter **2011**, 7(17), 7782-7789.

3. Gaps and Motivation: Why a New Instrument is Necessary

Critical Need: To more accurately determine pure shear and dilatational interfacial kinematics by systematic and controllable processing of interfaces

Langmuir trough[1] (dilation & shear)



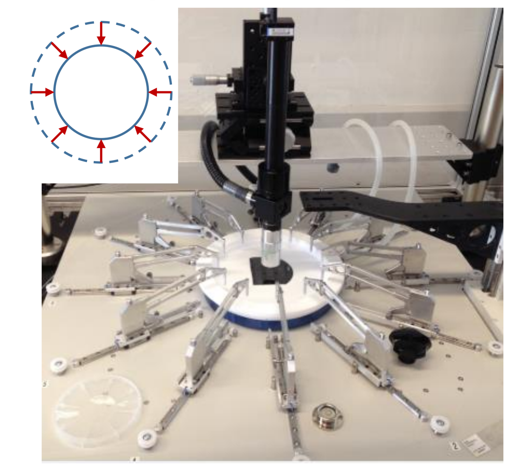
Interfacial viscoelastic moduli (K , G) convoluted with static compressibility $\Pi_{\alpha\beta}(\Gamma)$, creates orientation dependence of interfacial tension probe. As a result, there difficulty in determining parameters due to coupled shear and dilatational flows.

$$\Pi_{\parallel} = \Pi_{\alpha\beta}(\Gamma) - (K + G) \cdot \ln(J)$$

$$\Pi_{\perp} = \Pi_{\alpha\beta}(\Gamma) - (K - G) \cdot \ln(J)$$

$$J = \frac{A}{A_0}$$

Radial trough[2] (dilation)



Instrumentation is created for pure dilation/compression, but unable to 'pre-shear' interface and investigate interfacial structure

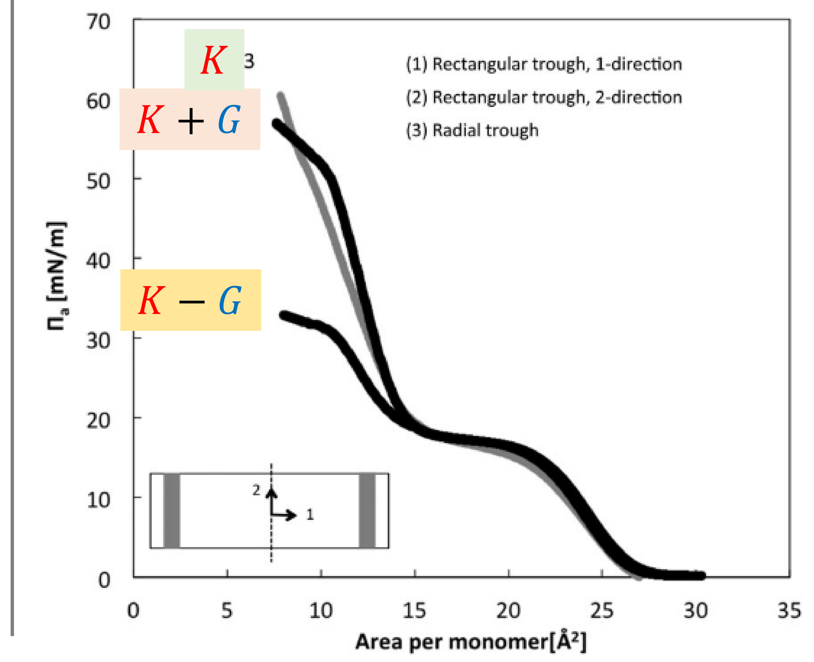
Finite elasticity

$$\Pi_{iso} = \Pi_{\alpha\beta}(\Gamma) - K \cdot \frac{\ln(J)}{J}$$

Example System: poly(*tert*-butyl methacrylate) on air-water interface

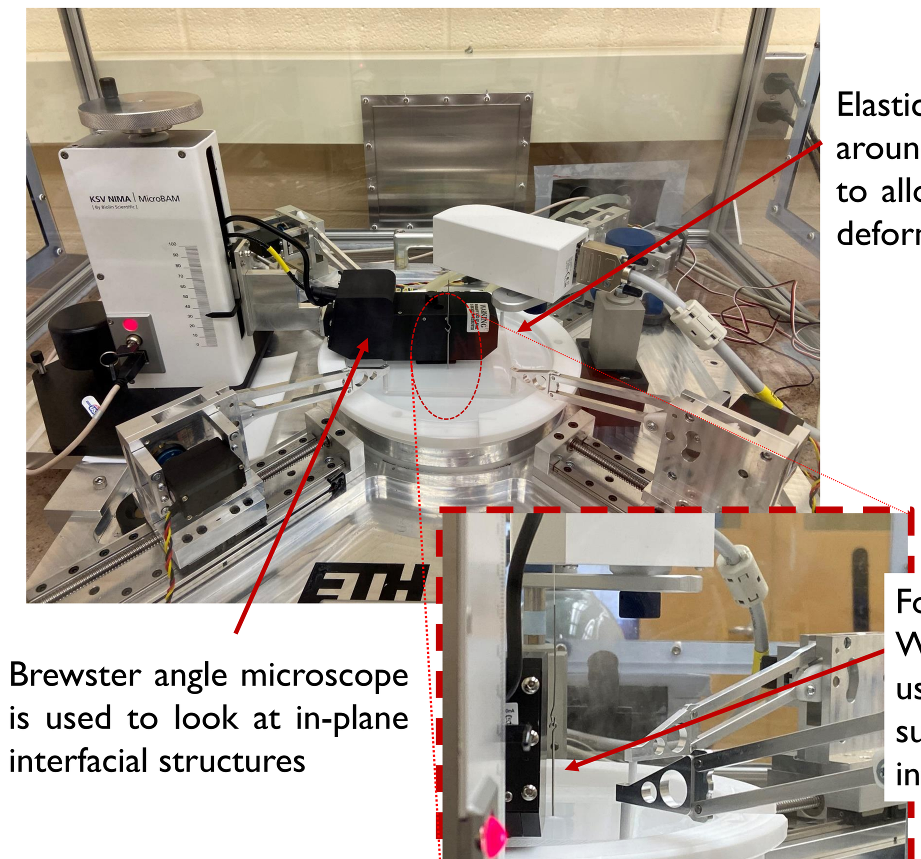
Surface pressure-area 'isotherm' on same interface show differences due to types of flow fields during dilation/compression

Pepicelli, M. et al. *Soft Matter* **2017**



[1] Verwijlen, T. et al. *Adv. Colloid Interface Sci.* **2014**, *206*, 428–436.
[2] Pepicelli, M. et al. *Soft Matter* **2017**, *13* (35), 5977–5990.

4. Quadrotrough Design



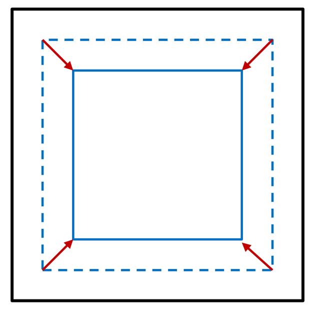
Elastic band is stretched around four step motors to allow precise interfacial deformation

Brewster angle microscope is used to look at in-plane interfacial structures

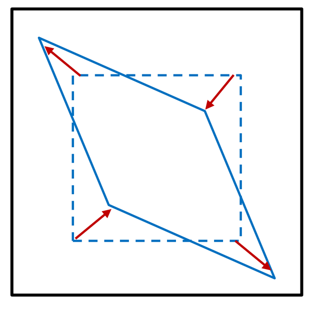
Force balance and Wilhelmy rod/plate used to measure the surface tension at the interface

Interfacial deformation modes

Pure Dilation



Pure Shear Strain



Quadrotrough has the ability to control the processing of the interface through pure shear and pure dilation/compression for better approximation of interfacial rheological parameters

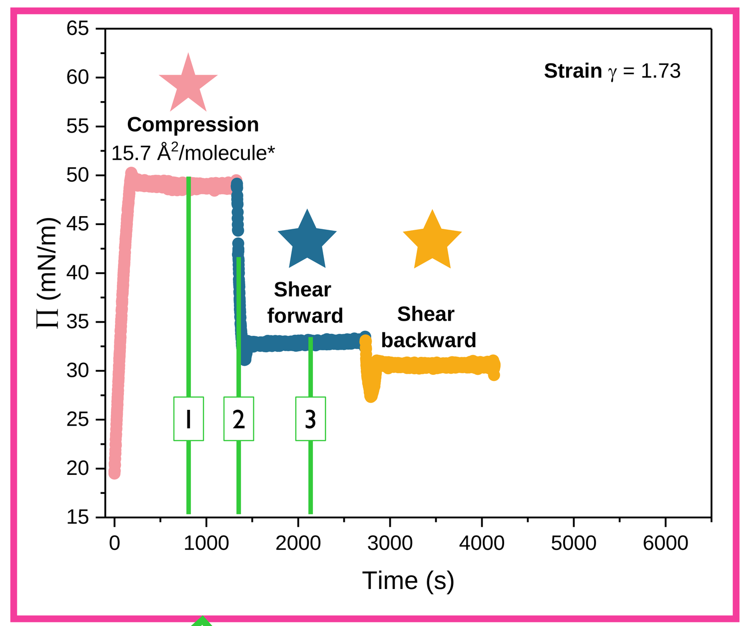
5. Impact of Interfacial Processing on Interfacial Structure and Rheology

Systematic processing of the interface allows more accurate decoupling of rheological and thermodynamic contributions for viscoelastic interfaces to determine true rheological parameters

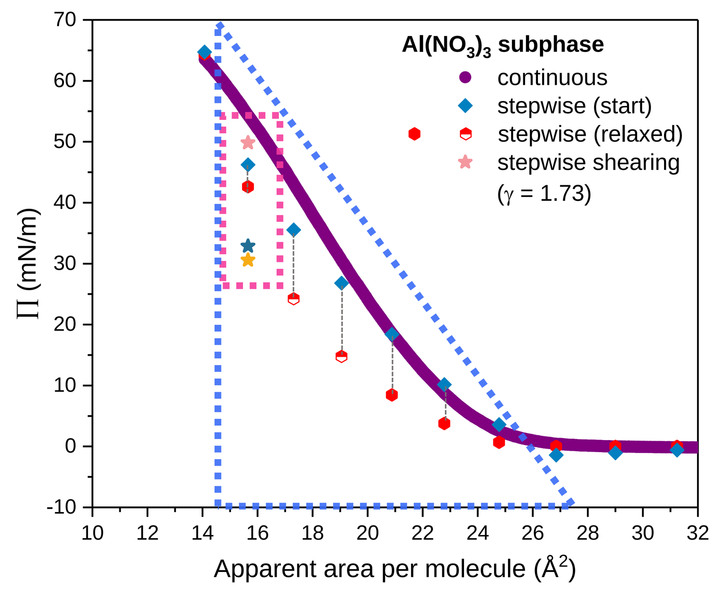
Model viscoelastic system: stearic acid on 10^{-4} M alumina nitrate subphase

5.1 *Interfacial Processing by Shear*

Shearing at desired area is a unique capability of the Quadrotrough to 'preshear' process the interface

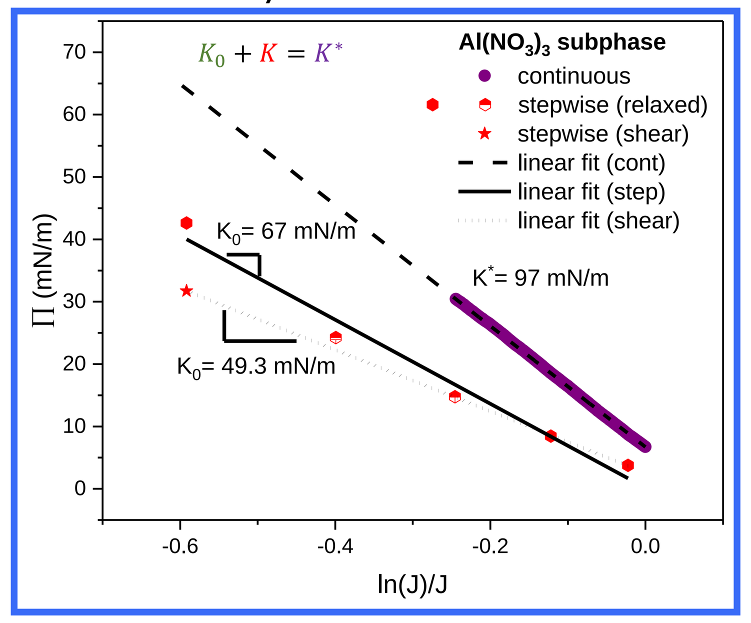


Continuous compression (1mm/min): rheological and thermodynamic
Stepwise compression: thermodynamic
Shearing: interfacial processing

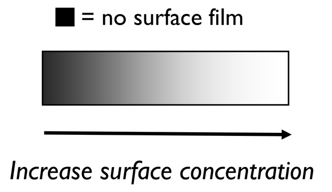


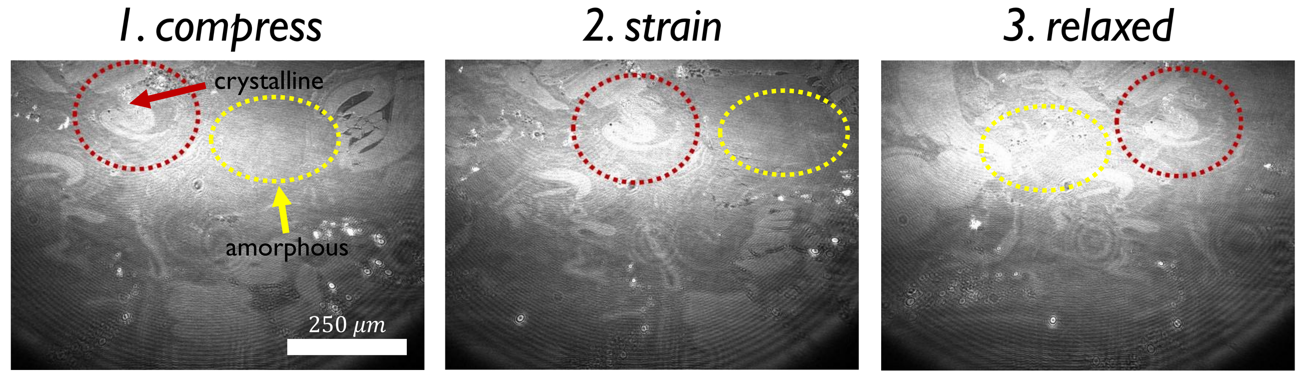
5.2 *Viscoelastic moduli determination*

The static 'thermodynamic' modulus determined from step compression (**67 mN/m**) is **not a true state variable** due to a metastable arrest. Upon shearing, the modulus decreases to **49.3 mN/m**, which is the **true state** of the system.



5.4 *Brewster angle microscope images*





Under shear, no breakup of crystalline structure, but evidence shows an image intensity change speculated to be due to amorphous structural rearrangement.

6. Conclusion/Future Work

- Pure shear and pure dilation can be achieved through new Quadrotrough instrument to allow processing protocols
- More accurately determine shear and dilatational rheological parameters and thermodynamic state variables with pure deformations
- Microstructure determines the macroscopic rheological behavior of viscoelastic interfaces as shown in literature and model stearic acid system.
- Currently, we are also implementing this sample environment on a neutron reflectometer, or *rheo*-MAGIK, for microscopic structural analysis

7. Acknowledgements

Wagner Group

NIST
Cedric Gagnon
Guangcui Yuang

ETH Zürich
Vermant Group
Damian Renggli
Christian Furrer
Martina Pepicelli
Alexandra Alicke