Measurements of Surfactant Squeeze-out Using Magnetically-Levitated Liquid Bridges

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EDGAR DEGAS
L'etoile [La danseuse sur la scene]

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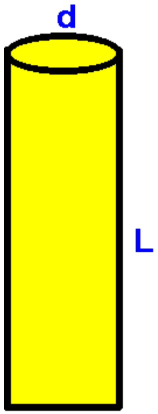
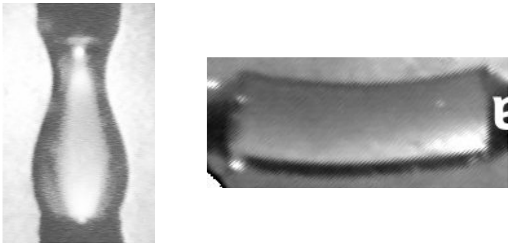
Liquid Bridges

- Liquid bridges: Columns of liquid supported by two solid surfaces — These are generally opposing right circular cylinders in 0g.



- For a *cylindrical* bridge of length *L* and diameter *d*, in zero g, the maximum slenderness ratio Λ [L/d] = π [Rayleigh]

- In the presence of gravity the cylindrical shape of an axisymmetric bridge tends to deform (see our work **J. Coll. Int. Sci. *213*, 592 (1999)**)



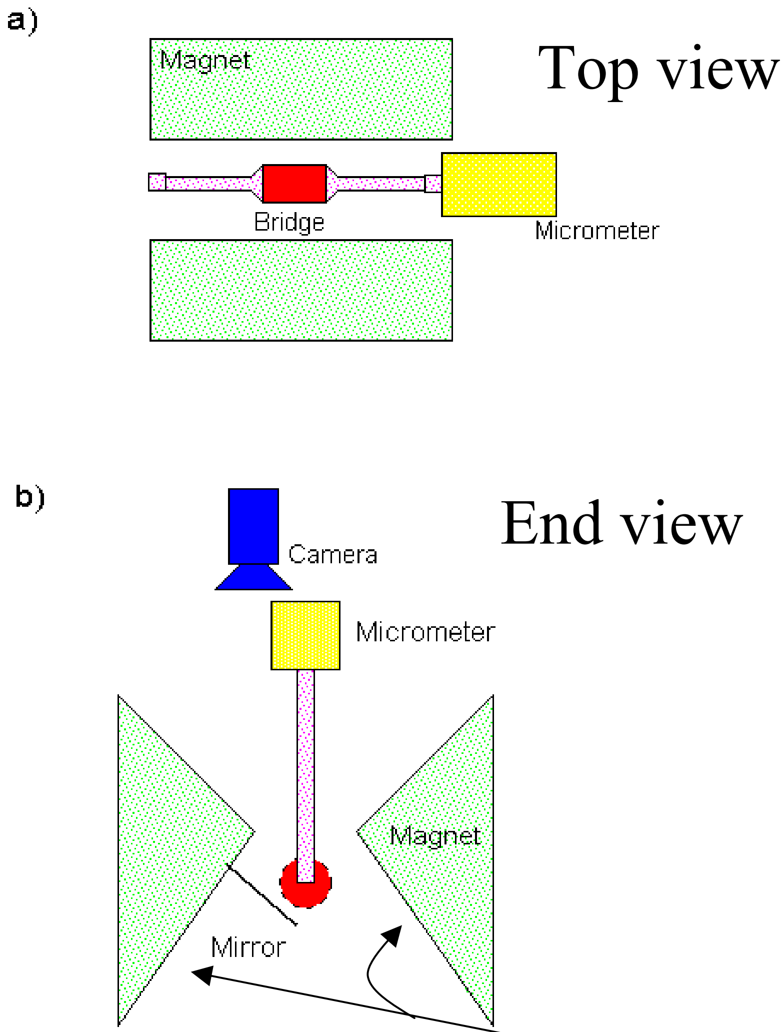
Principles of magnetic levitation

(see our work in **Phys. Fluids 10, 2208 (1998)**)

- Fluid has a volumetric magnetic susceptibility χ. On applying field H:
- Energy per unit volume is $U = -\frac{1}{2}\chi H^2$ ➔
- **Force per unit volume is $F = -\nabla U = \frac{1}{2}\chi \nabla H^2 = \chi H \nabla H$. This force can be oriented to counteract gravity.**
- Dissolve paramagnetic manganese chloride tetrahydrate in water or glycerol to create highly paramagnetic fluid that can be controlled with a relatively small field.

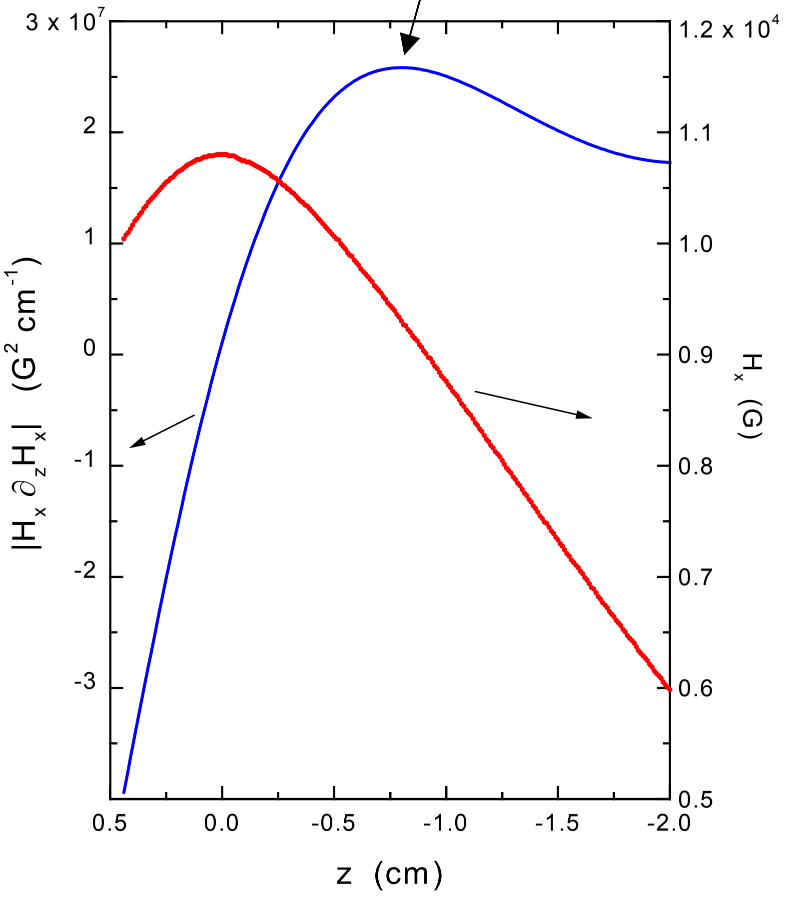
Thus the effective body force on the column may be controlled by varying the current in the magnet — as a function of time!

Apparatus



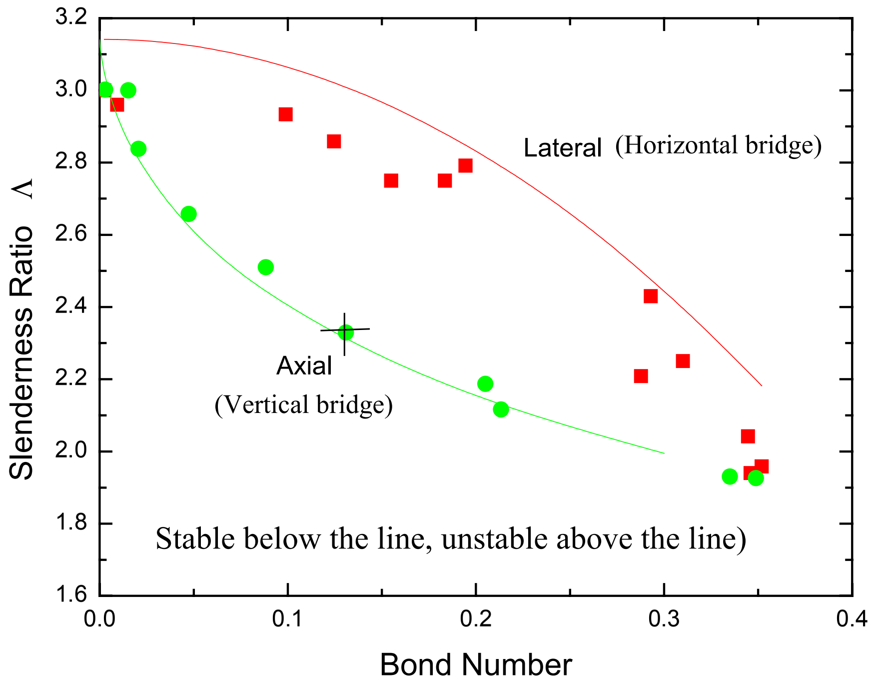
“Faraday pole pieces” create uniform *force*

Region of quasi-uniform force

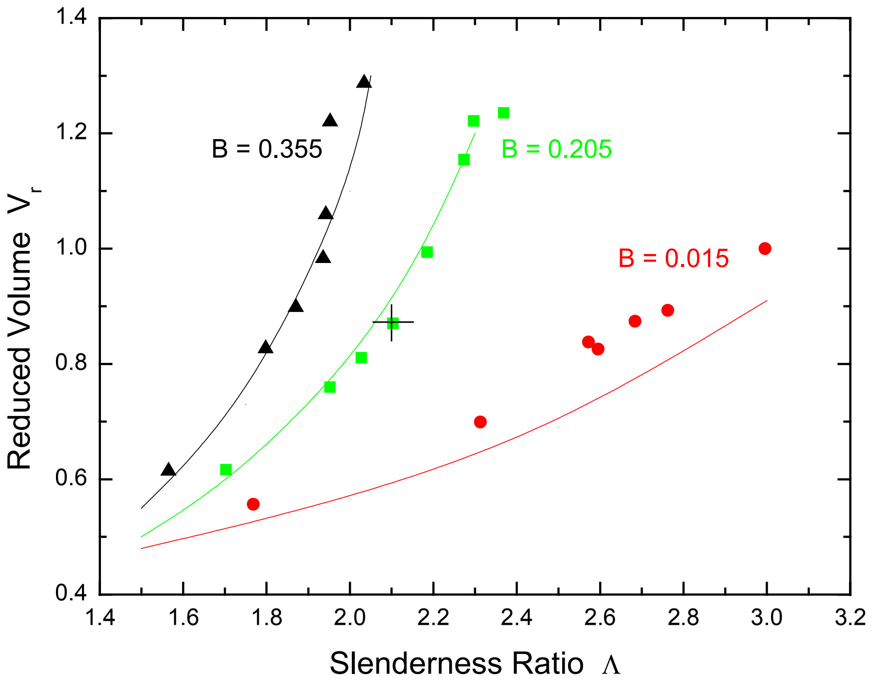


H and H∇H profiles

We have looked at stability issues



Stability of cylindrical bridges (V_r=1) vs. Bond number



Stability curves as function of V_r at fixed Bond number(s)

Bond number: $B \equiv \dfrac{\left(\rho g - \tfrac{1}{2}\chi \nabla H^2\right) d^2}{4\sigma}$

Ratio of gravitational force
to surface forces

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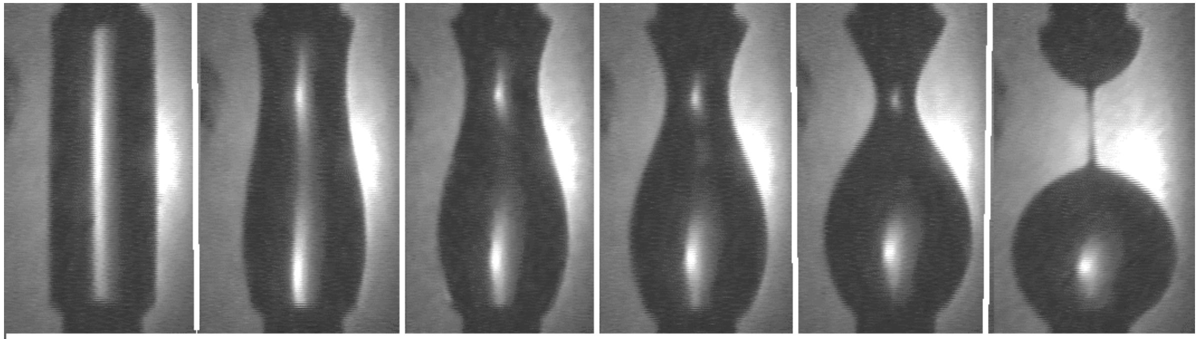
We have looked at collapse dynamics

Glycerol + manganese chloride tetrahydrate



t = 0　t = 5 s　t = 10 s　t = 15 s　t = 20 s　t = 24 s

Sequence of images of a glycerol bridge after the upward magnetic force is reduced suddenly. Bridge collapses over time due to gravity. t corresponds to time, in seconds

Movie may be viewed at

http://liq-xtal.case.edu/Videos.htm

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We have looked at resonance behavior

Vary the total body force sinusoidally at frequency ω and examine the response.

First, set *time averaged* Bond number B^{o}_{eff} by applying appropriate d.c. current i_o, and therefore $H\nabla H$…….

Then, modulate magnet current.

Force $\propto (i_o + \delta i \sin \omega t)^2$, and

$\delta B_{\mathrm{eff}} \propto 2 i_o\, \delta i \times \sin \omega t \; + O(\delta i^2) \sin^2 2\omega t$

Movie may be viewed at

http://liq-xtal.case.edu/Videos.htm

Dynamic surface tension

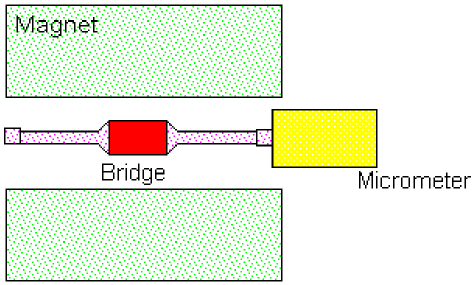
The change of surface tension with time as surfactant molecules move between the surface and bulk

Motivation: Investigate "respiratory distress syndrome" in neonates.

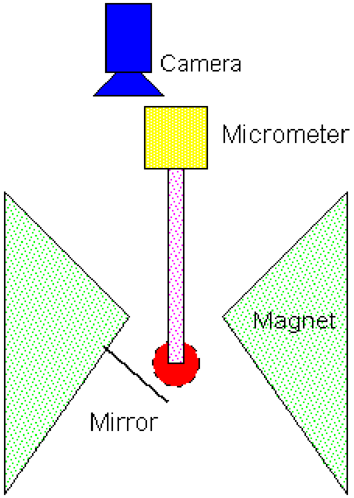
- During respiration alveoli to grow and shrink periodically
- This requires *dynamic* variation of surface tension to balance $\Delta P = \frac{2\sigma}{R}$
- Premature infants have not manufactured sufficient surfactant (e.g., phosphatidylcholine). Thus their pulmonary fluid cannot respond properly during breathing.

Use horizontal bridge to determine “squeeze-out time” of surfactant from surface.

a) Top View



b) Side View



As a function of surfactant concentration:

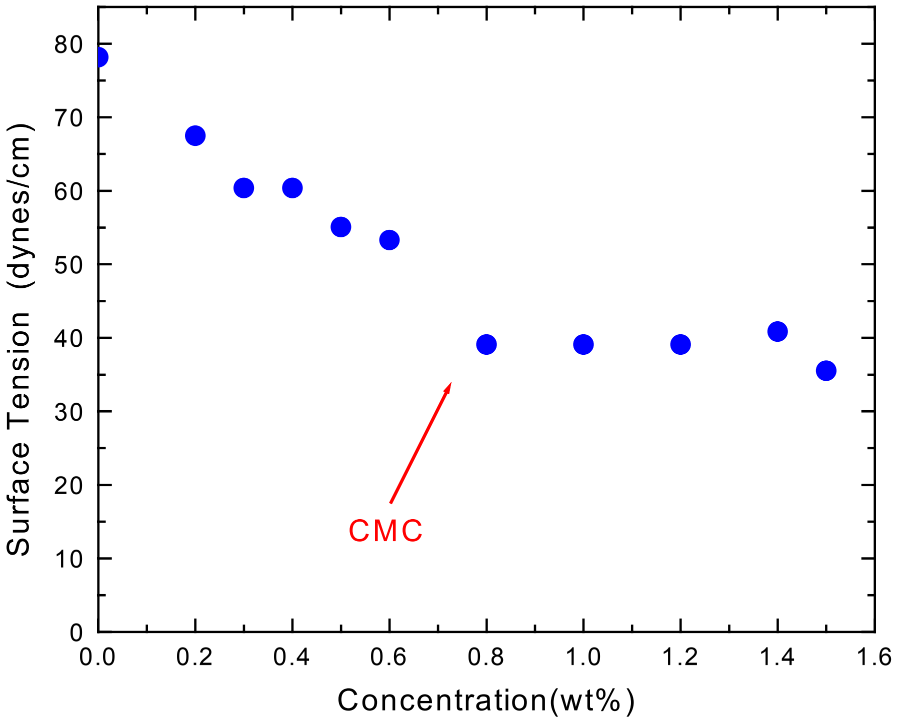
Rapidly reduce bridge length in zero gravity

Examine the ***electrical resistance vs. time*** of the bridge when the lateral area of the bridge is reduced suddenly. (In zero effective gravity the only relevant force is surface tension)

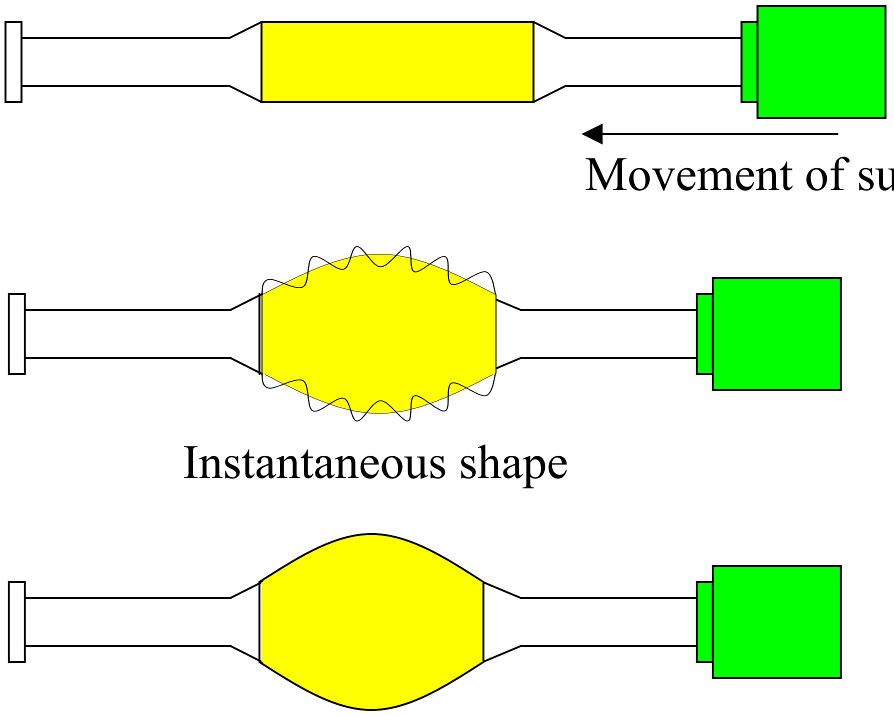
- Mixtures of paramagnetic liquid ($MnCl_2 \cdot 4H_2O$/Water)
- Add Dodecyl trimethyl ammonium chloride (cationic surfactant)

  $0 \leq X \leq 1.5$ wt. %.

- Critical Micelle Concentration (CMC) is determined from surface tension measurements using capillary rise technique. (Above CMC additional molecules tend to form micelles rather than adsorb at the surface)



- For each concentration X of surfactant, bridges of $\Lambda = 2.5$ are created.
- A rapid change of length (1.3 mm in 500 ms) forces it to assume a new shape.



Movement of support rod

Instantaneous shape

Final shape as $t \to \infty$

There is a transient buckling of the surface after the bridge is “squished” in order to accommodate the surfactant that has not yet gone from the surface into the bulk. As surfactant is squeezed-out into bulk, the surface area of the bridge is reduced to the final equilibrium shape

Crenellations are due to:

- Induced capillary waves during “squishing”
- Accommodation of surfactant that cannot be squeezed out from surface instantaneously when the bridge area is reduced during “squishing”

The relaxation time of the crenellations for large X ***is related to the squeeze-out time of the surfactant, and therefore to the response time of the (dynamic) surface tension.***

This relaxation time is determined experimentally by the relaxation of electrical resistance across the bridge $R = \rho L/A$

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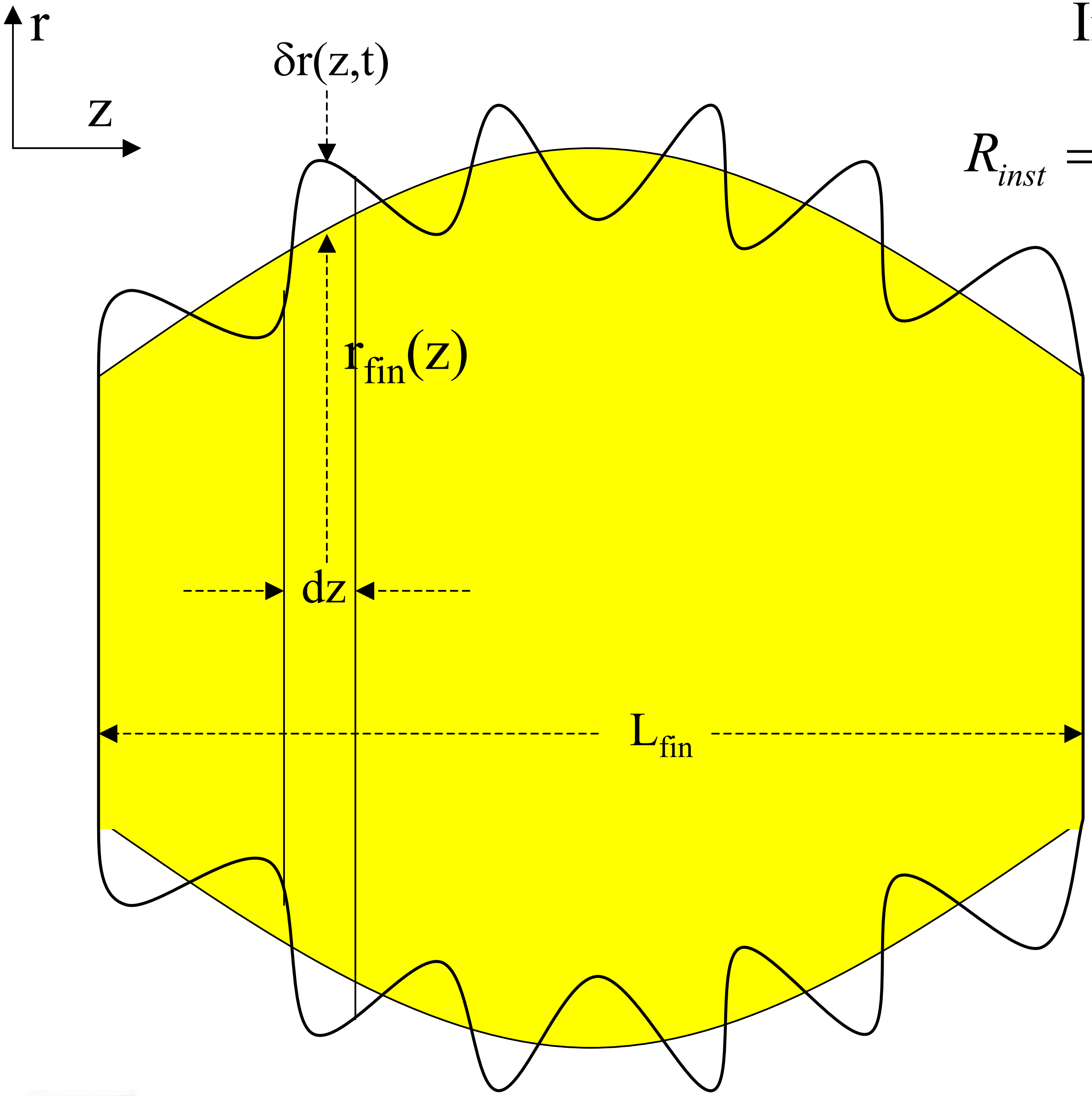


Instantaneous resistance:

$$R_{inst} = \int_{z=0}^{L_{fin}} \frac{\rho}{\pi\left[r_{fin}(z) + \delta r(z,t)\right]^2} dz$$

Final resistance:

$$R_{fin} = \int_{z=0}^{L_{fin}} \frac{\rho}{\pi r_{fin}^2(z)} dz$$

We can see that $R_{inst} > R_{fin}$:

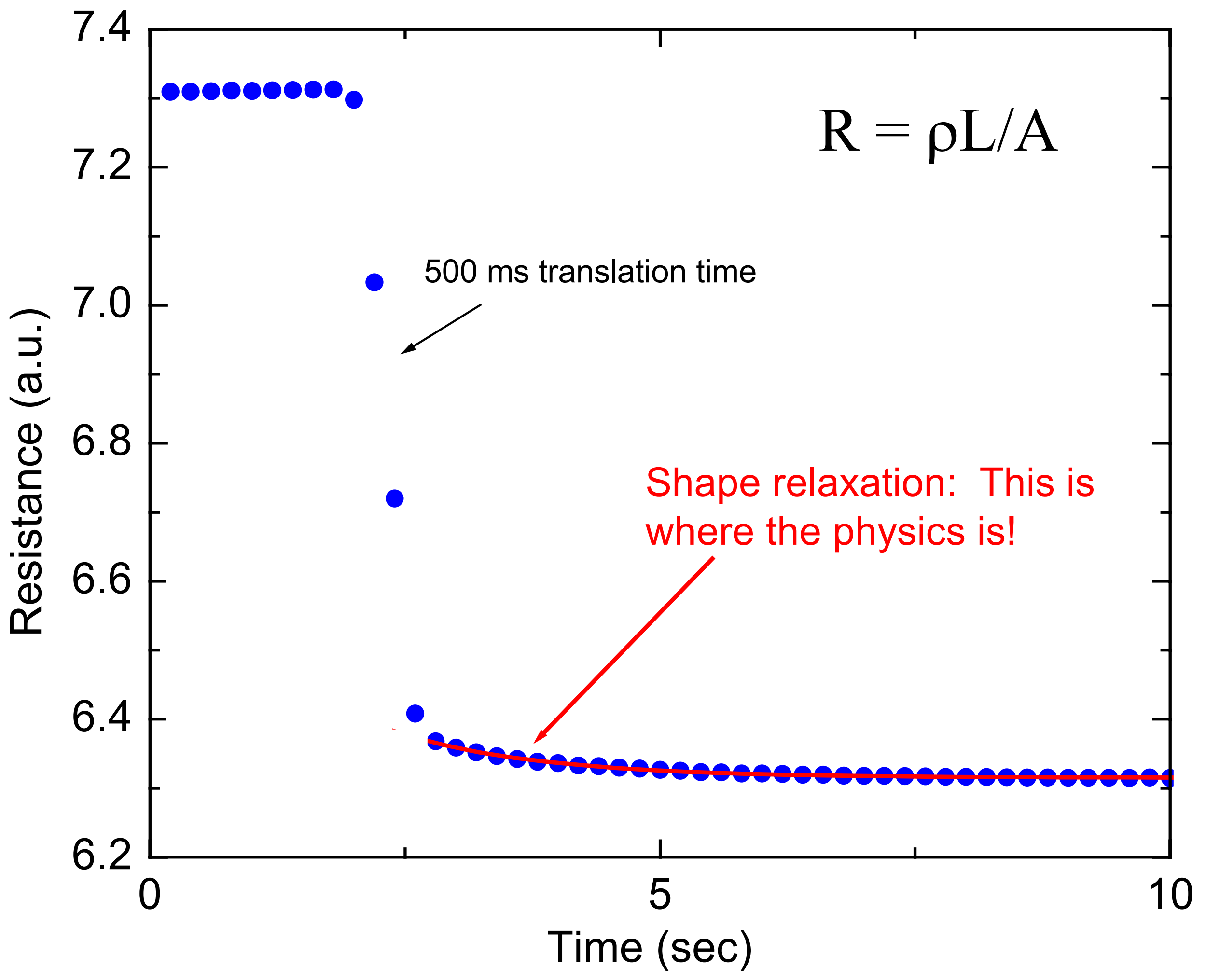
Expand R_{inst} in powers of $\delta r(z,t)$, from which

$$R_{inst} = \int_{z=0}^{L_{fin}} \frac{\rho dz}{\pi r_{fin}^2(z)} + \int_{z=0}^{L_{fin}} \frac{\rho}{\pi r_{fin}^2(z)} \left[-2\frac{\delta r(z,t)}{r_{fin}(z)} + 3\left(\frac{\delta r(z,t)}{r_{fin}(z)}\right)^2 + -4\left(\frac{\delta r(z,t)}{r_{fin}(z)}\right)^3 + 5\left(\frac{\delta r(z,t)}{r_{fin}(z)}\right)^4 - +\ldots \right] dz$$

1. Even order terms all have positive coefficients
2. From volume conservation, local negative $\delta r(z)$ terms are larger than local positive $\delta r(z)$ terms

$\Rightarrow R_{inst} > R_{fin}$

Resistance vs. Time



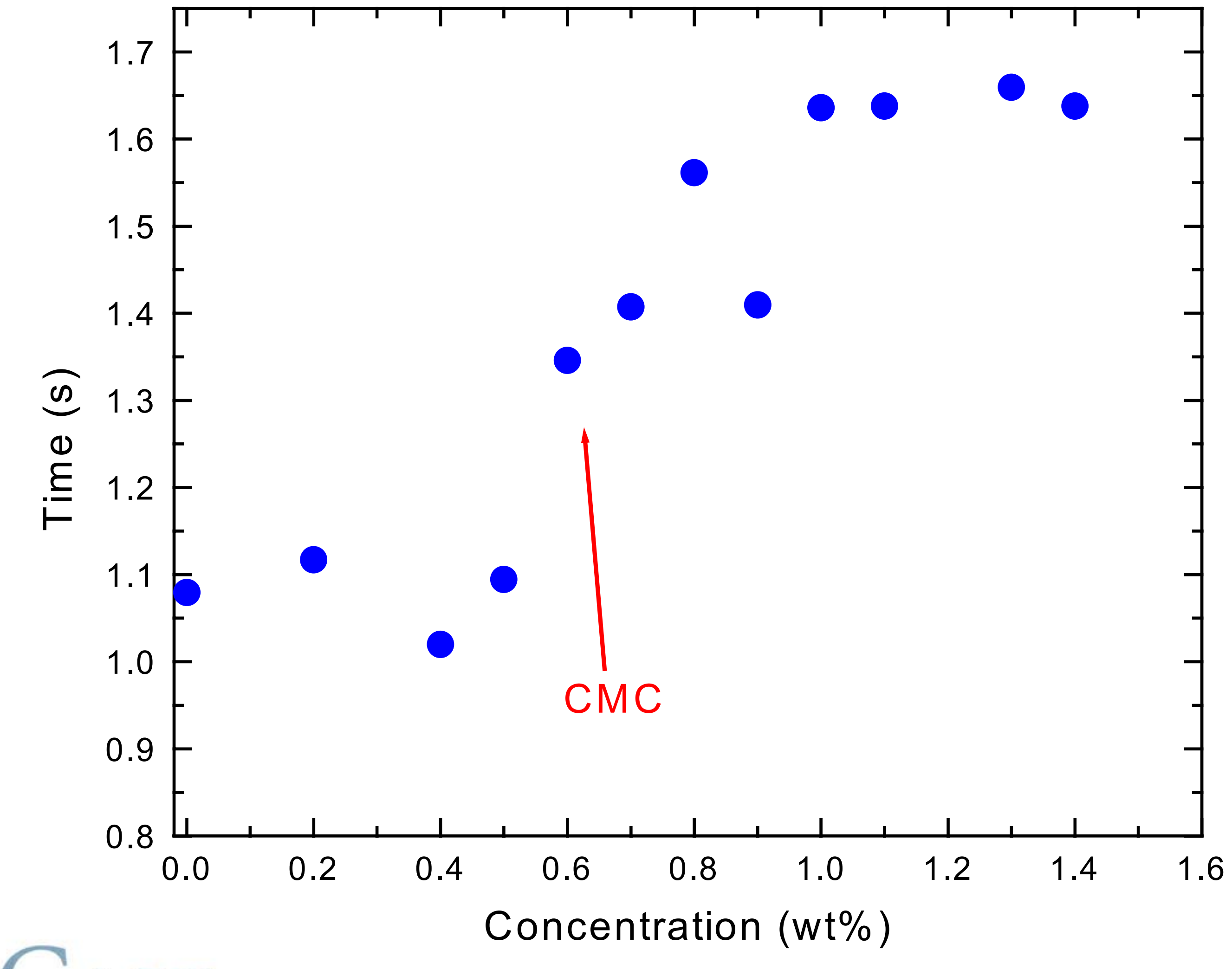
$R = \rho L/A$

500 ms translation time

Shape relaxation: This is where the physics is!

τ vs. X

For each concentration we obtain
the relaxation time



For low concentrations, X < CMC (τ ~ 1.1 s)

- Surface area ***decreases*** on translation of rod. Increased surfactant density at surface ***can*** be accommodated by surface due to its small surface density. There is no need for surfactant to be pushed into bulk.

- Fast capillary waves (> 8 Hz) are induced by the vibration during squishing and result in high electrical resistance. (We measure the envelope decay)

- As capillary waves decay, electrical resistance decreases to final equilibrium value (associated with final equilibrium shape)

So, for small X, we measure the decay of capillary waves, not of surfactant squeeze out

For large concentrations X > CMC (τ ~ 1.7 s)

- Capillary waves are damped very rapidly for X > CMC, *and do not contribute to measured signal during decay.*

- When rod translates, surface cannot rapidly accommodate the higher surfactant density ➔ surface area is temporarily > equilibrium surface area.

- Surface area relaxes from near equilibrium to equilibrium shape as surfactant is squeezed out from surface. Resistance relaxes with surface topography, where τ is the squeeze-out time of surfactant.

- This is ***not*** a diffusion limited process, which is about four orders of magnitude faster.

Take home message:

Magnetic levitation has numerous applications in studies of fluids, “soft” and “hard” condensed matter physics, and biophysics

1. “Dial in” appropriate gravitational field, e.g., Martian, Lunar
2. The field can be maintained indefinitely
3. Field can be varied with time

Collaborators

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