Dissipation Mechanisms in Bubble Scale Foam Rheology

Departures from Princen's Sheared Honeycomb

P. Grassia[1], B. Embley[1], C. Oguey[2]

[1]CEAS
University of Manchester

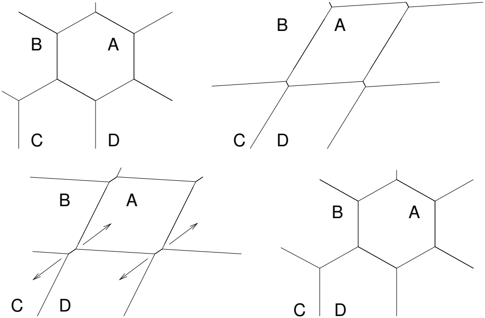
[2]LPTM
University of Cergy-Pontoise

Outline

Outline

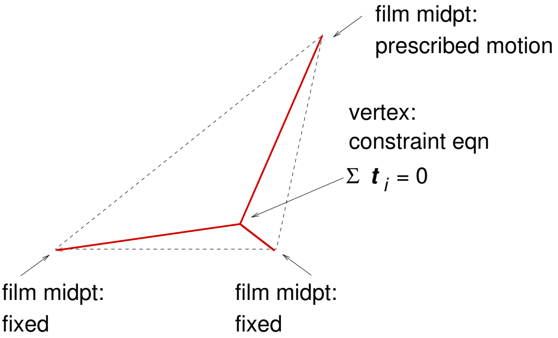
Princen's honeycomb

late 1970s through 1980s, plus several reviews



Under shear, system undergoes *topological transformation*
– so called 'T1'

Unit cell of Princen honeycomb



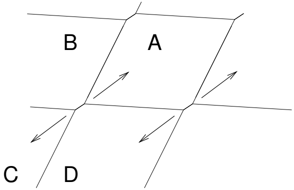
Quasistatic mechanical equilibrium configuration given vertex locations for unit cell

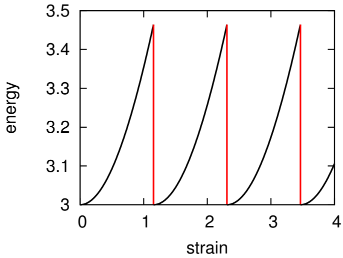
Vertex = *Fermat-Steiner* point

Films meet at $\frac{2\pi}{3}$ angles

Princen model at topological transformation

Departures from mechanical equilibrium



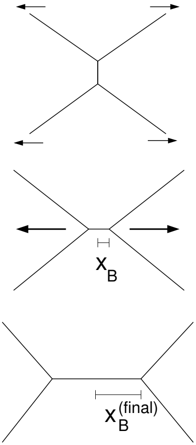


Princen structure undergoes a *discrete* jump at topological transformation

How attempt to model the dissipative out-of-equilibrium relaxation process?

Outline

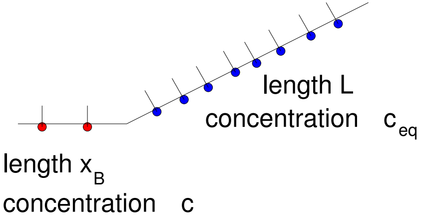
Relaxation to mechanical equilibrium
Durand and Stone model



- Quasi-static model instantaneous jump to $x_B^{(final)}$
- *Dynamic* model describes how the (half)length x_B of *newly created film* evolves with time t, in presence of surface viscosity μ_s, film tension γ_{eq} and Gibbs elasticity $\bar{\Gamma}$
- Evolution time scale set by ratio μ_s/γ_{eq}, but influenced by $\bar{\Gamma}$

Surfactant conservation

Durand and Stone



Surfactant surface concn evolves as $c(t)$ in growing film (*assumed* spatially uniform), and (*by assumption*) constant c_{eq} everywhere else

Global conservation implies

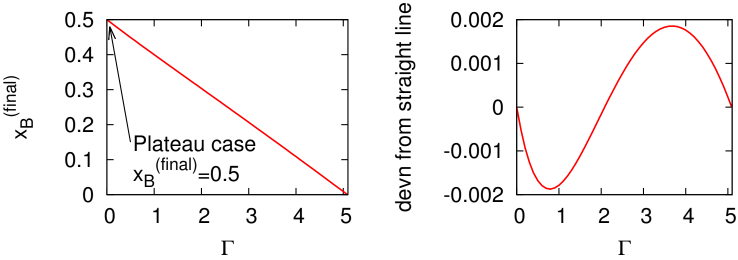
$$c(t)x_B(t) + c_{eq}L(t) = c_{eq}L_c$$

where L_c is the *initial* value of $x_B + L$

Final mechanical equilibrium state

Durand and Stone

Surfactant *concn* on newly created film ↓ with time,
Tension on newly created film ↑ with time:
Mechanical force balance when $x_B = x_B^{(final)}$

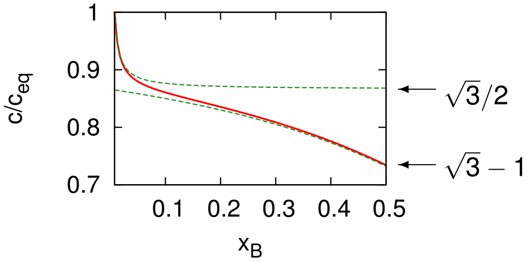


If Gibbs parameter $\bar{\Gamma}$ ↑, more elastic (i.e. less compliant) films
→ Smaller $x_B^{(final)}$

Surfactant concentration
Durand and Stone

Surfactant coverage is related *directly* to geometry

$$c(t) = c_{eq}(L_c - L(t))/x_B(t)$$

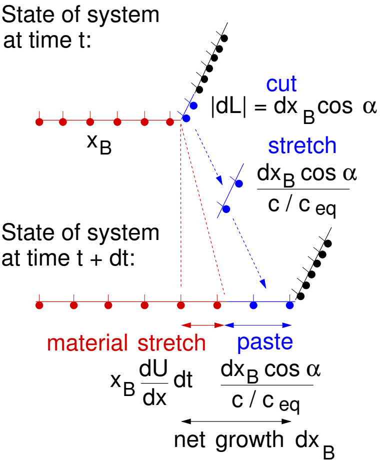


$c(t)$ deviates from c_{eq} *long before* $x_B(t)$ becomes significant

Surfactant transferred *onto* newly created film from neighbours overwhelming any surfactant that is originally there

Film stretch rates

A consequence of inter-film surfactant transfer



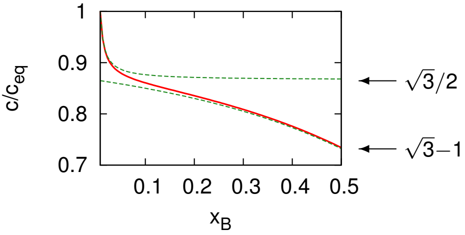
$\partial U/\partial x$ is stretch rate of film *material elements*, whereas $\dot{x}_B/x_B$ is net stretch rate of film *vertex geometry*

$\partial U/\partial x$ is *not* the same as $\dot{x}_B/x_B$

Vertex must *slip* relative to film material points

Amt of slip depends on angle α between films and on c/c_{eq}

Comparison between $\partial U/\partial x$ and $\dot{x}_B/x_B$



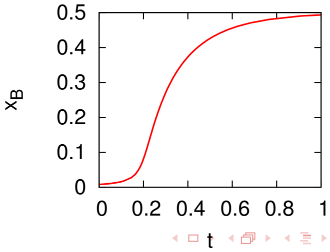
For small x_B, with angle α between growing/shrinking films

$$\frac{\partial U}{\partial x} \approx \left(1 - \frac{\cos\alpha}{c/c_{eq}}\right)\frac{\dot{x}_B}{x_B}$$

$$\dot{x}_B/x_B \gg \partial U/\partial x$$

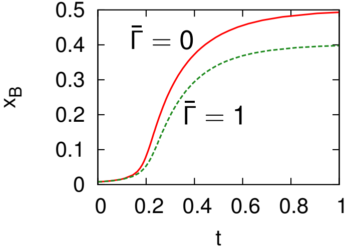
even for $x_B \ll 1$

x_B exhibits *rapid initial acceleration*

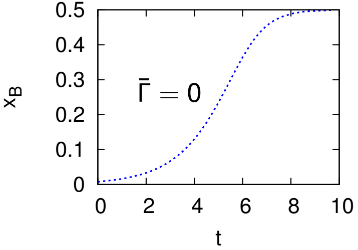


Effect of rapid initial acceleration

Durand and Stone



$\dot{x}_B / x_B \gg \partial U / \partial x$
for Durand and Stone



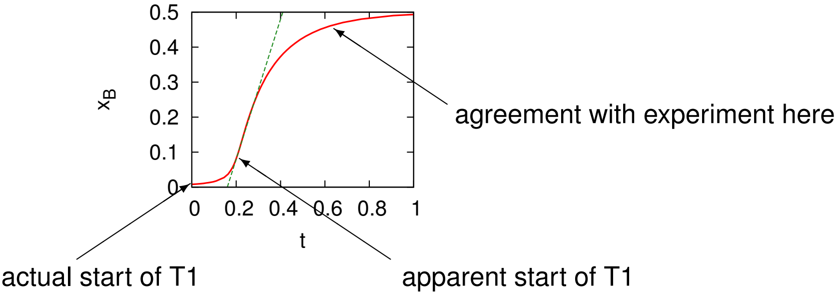
Contrast model of Biance et al. (2009)

Assumes $\dot{x}_B / x_B = \partial U / \partial x$

Exhibits *very slow* evolution (note very different time scale cf. Durand and Stone graph)

Evolution of film length – Experimental observations
Durand and Stone

Rapid motion (*after* initial acceleration) easiest to detect in expt



Summary and conclusions

Out of mechanical equilibrium foams

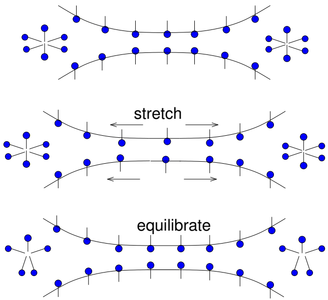
- Simple (but elegant) model for evolution of x_B in T1 process
  - Considers surfactant exchange *between* films (i.e. vertex *slips* relative to film material points), but ignores other (longer time scale) surfactant equilibration processes (Hence *unequal* tensions in 'final' state)
- Surfactant coverage c related directly to geometry x_B
- Abrupt change in c even whilst new film is very short ($x_B \ll 1$)
  - *Rapid initial acceleration* of x_B

Outline

1. Hexagonal honeycomb foams
2. Foams out of mechanical equilibrium
3. Foams out of physicochemical equilibrium

Surfactant transport in thin foam films

Consider film stretched by T1 and/or imposed shear



- Durand and Stone ‘final’ state has *unequal* film tensions
- Equilibrium surfactant concentration only restored from bulk over some (longer) characteristic time τ
- Equilibration is dissipative: decay of *chemical potential*

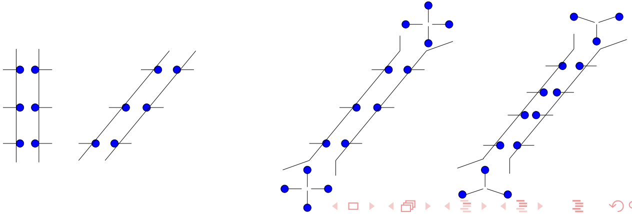
Out of physicochemical equilibrium foams

Cantat (2011) model

Consider shear of e.g. a hexagonal honeycomb foam with shear strain s (affecting film length L) applied at a rate comparable with physicochemical relaxation rate τ^{-1}

$$\frac{dc}{dt} = -\frac{\dot{s}}{L}\frac{dL}{ds}c - \frac{(c - c_{eqm})}{\tau}$$

$$\left(\begin{array}{c}\text{shear induced}\\ \text{film stretch}\end{array}\right) \quad \left(\begin{array}{c}\text{equilibration}\\ \text{with reservoir}\end{array}\right)$$



Deborah number

Physicochemical analogue of capillary number

$$De = \dot{s}\,\tau$$

- Controls departure from physicochemical equilibrium
- $De \gg 1$: *strong* departure from physicochemical equilibrium

  (Total surfactant on film *conserved* during shear flow)
- $De \ll 1$: *weak* departure from physicochemical equilibrium

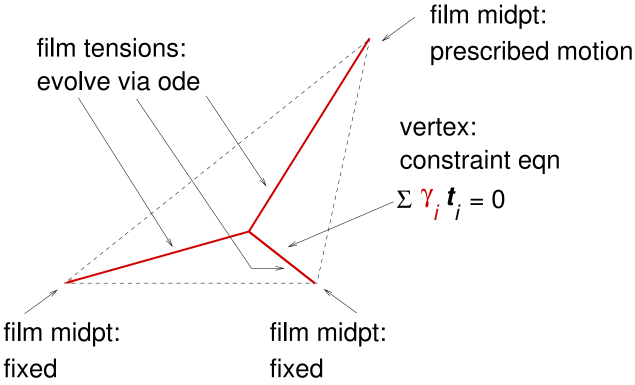
  (Near *Princenian* behaviour)

Unit cell in a honeycomb/staircase geometry

via Cantat's model

Mechanical relaxn rate $\gg$ Physicochemical relaxn rate

Regardless of *De*, foam *remains* in mechanical eqm



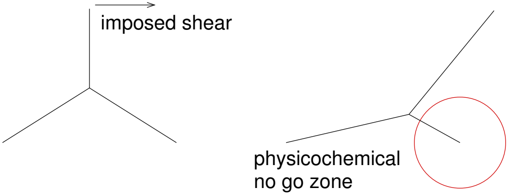
High Deborah number limit

Conserved surfactant: Suppression of T1

Linearised surface tension model $\gamma/\gamma_{eqm} = 1 - \bar{\Gamma}(c/c_{eqm} - 1)$
becomes, for *conserved* surfactant coverage
$$\gamma/\gamma_{eqm} = 1 - \bar{\Gamma}(L_{eqm}/L - 1)$$

If $L/L_{eqm} \downarrow$, then $\gamma/\gamma_{eqm} \downarrow$,
preventing further decrease in L/L_{eqm}: T1 is *suppressed*

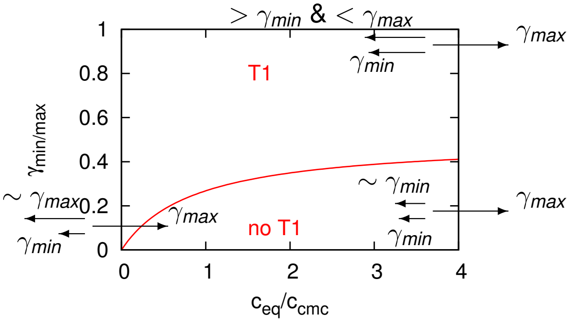
$\rightarrow$ Secular film growth to bursting point?



Phase diagram for T1s

Two parameter surface tension model in the high *De* limit

Consider instead tension model with finite cutoff γ_{min} at cmc

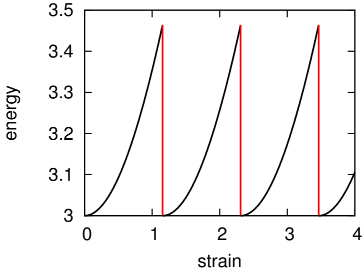


Always have T1 if $\gamma_{min/max} \geq \frac{1}{2}$

T1 is more likely if concn ratio c_{eq}/c_{cmc} is small

Low Deborah number limit

Near Princenian behaviour



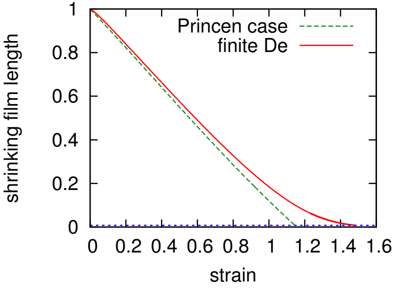
Near agreement with Princen's model away from T1, punctuated by *non-Princenian* behaviour near T1

Non-Princenian effects:
can be *physicochemical* in origin, not just mechanical;
can occur immed. *before* T1, not only immed. after T1

Deviation from Princenian film length relations

Pre-T1

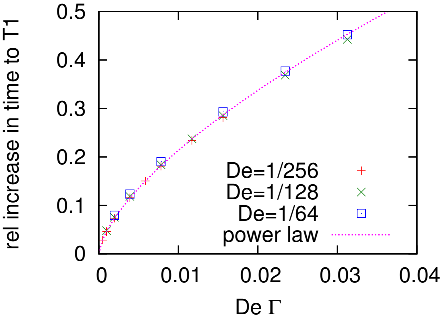
For Princen, shrinking film length nearly linear in applied strain



Large *relative* changes in film length on approach to T1
Surfactant concentration grows $\longrightarrow$ Surface tension falls
Decay of film length is offset $\longrightarrow$ T1 is delayed

Delay in T1

Delay in T1 depends on Deborah number *De*
and on surface tension variation parameter $\bar{\Gamma} = |d\gamma/dc|$



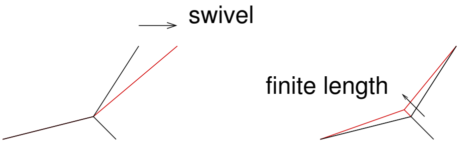
Bretherton-like $\frac{2}{3}$ power law behaviour

Implications of mechanical equilibrium relation

Net pull of long films weakens both due to *swivel* and due to *finite length* of shrinking film

Net pull of long films balances pull of shrinking film

$$1 - \gamma_{shrinking} \sim (s - s_{Princen}) + L_{shrinking}$$

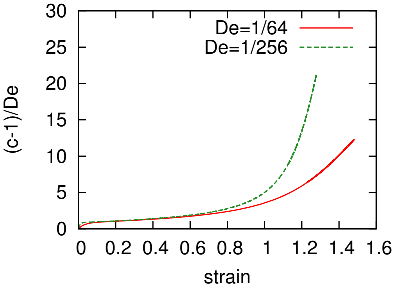


Concentration in shrinking film rises *above* equilibrium to match weakening net pull

Surfactant coverage on shrinking film

Evolution of surfactant coverage (and hence film length) depends on deviation from equilibrium of shrinking film

$$De\frac{d(c\,L)}{ds} = L(c_{eqm} - c) \longrightarrow \frac{c}{c_{eqm}} \approx 1 + \frac{De}{L}\left|\frac{dL}{ds}\right|$$

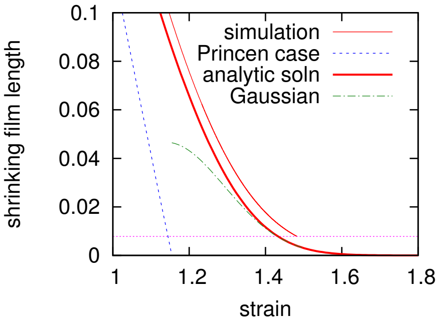


Concn deviation $c - 1$ grows from $O(De)$ to $O(De^{1/2})$ but remains small
$\longrightarrow$ Isotherm can be *linearised*

Both $1 - \gamma_{shrinking}$ and $s - s_{Princen}$ also $O(De^{1/2})$

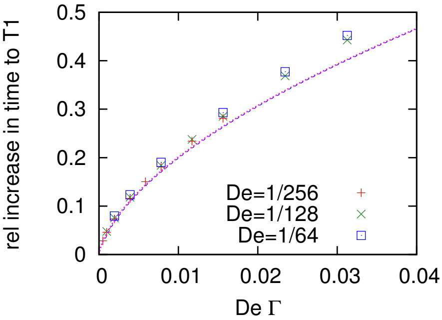
Predicted film length evolution – Analytic solution

Zoom in near the Princen strain s_P



$$L = \frac{2\sqrt{\bar{\Gamma}\, De}}{1 + \operatorname{erf}\left((s - s_P)/\sqrt{\bar{\Gamma}\, De}\right)} \exp\left(-\frac{(s - s_P)^2}{\bar{\Gamma}\, De}\right)$$

Predicted delay in T1



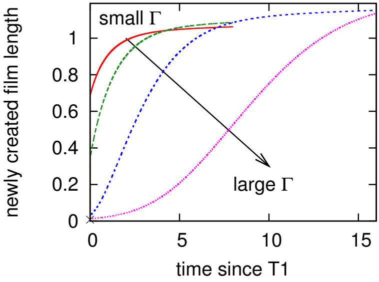
T1 occurs as film length *L* falls to ε (liquid fraction parameter)

$$\text{delay in T1} = \sqrt{\Gamma\, De}\sqrt{\log(\sqrt{\Gamma\, De}/\varepsilon)}$$

No free parameters

After topological transformation
(low *De* limit only)

- New film created with length ε and then grows
- Mechanical relaxn *followed by* physicochemical relaxn
- Rel. amounts of each equilibration depend on $\bar{\Gamma} \equiv |d\gamma/dc|$

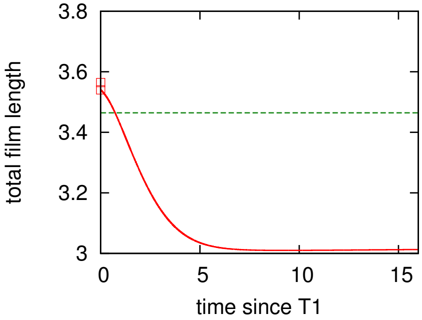


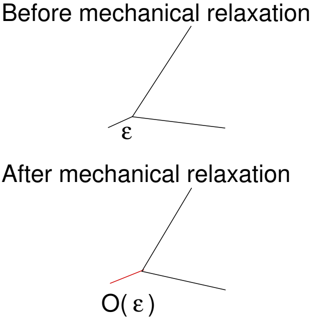
- Total film energy over *all* films relaxes

Post-T1 relaxation

Total film energy over all films

Large $\bar{\Gamma}$: minimal (instantaneous) mechanical relaxation; equilibration *entirely* physicochemical

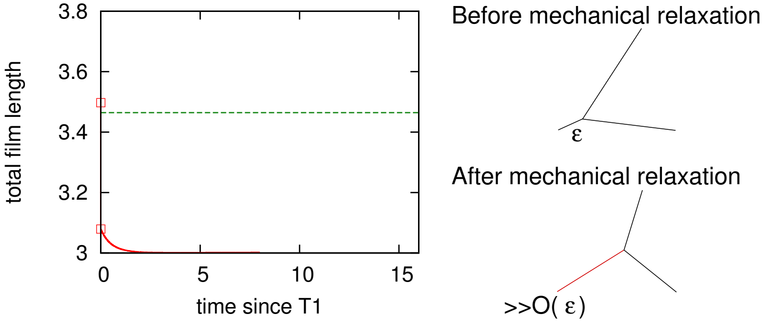




Post-T1 relaxation

Total film energy over all films

Small $\bar{\Gamma}$: significant *instantaneous* mechanical relaxation, followed by (relatively fast) physicochemical equilibration



Summary and conclusions

Out of physicochemical equilibrium foams

- Sheared staircase in *mechanical* equilibrium out of *physicochemical* equilibrium
- *Deborah number* controls departure from physicochemical equilibrium
- High Deborah number: strong *suppression* of topological transformations; instead secular growth/film bursting
- Low Deborah number: topological transformation *delayed* by an amount $\sqrt{De}$
- Low Deborah number: relaxation post-topological transformation can be entirely physicochemical, or can be part-mechanical, part-physicochemical