Dissipation Mechanisms in Bubble Scale Foam Rheology
Departures from Princen’s Sheared Honeycomb

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Outline

1. Hexagonal honeycomb foams
2. Foams out of mechanical equilibrium
3. Foams out of physicochemical equilibrium
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3. Foams out of physicochemical equilibrium
Under shear, system undergoes \textit{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

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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 $\mu_s$, film tension $\gamma_{eq}$ and Gibbs elasticity $\bar{\Gamma}$

Evolution time scale set by ratio $\mu_s/\gamma_{eq}$, 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 *conc* 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
\[ c(t) = c_{eq}(L_c - L(t))/x_B(t) \]

\[ \frac{c}{c_{eq}} \]

\[ x_B \]

\[ \sqrt{3}/2 \]
\[ \sqrt{3} - 1 \]

\( c(t) \) 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

\[ \frac{\partial U}{\partial x} \] is stretch rate of film **material elements**, whereas \( \dot{x}_B / x_B \) is net stretch rate of film **vertex geometry**

\[ \frac{\partial U}{\partial x} \] is **not** the same as \( \dot{x}_B / x_B \)

Vertex must **slip** relative to film material points

Amt of slip depends on angle \( \alpha \) between films and on \( c / c_{eq} \)
Comparison between $\frac{\partial U}{\partial x}$ and $\frac{\dot{x}_B}{x_B}$

For small $x_B$, with angle $\alpha$ between growing/shrinking films

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

$\dot{x}_B/x_B \gg \frac{\partial U}{\partial x}$
ev-en for $x_B \ll 1$

$x_B$ exhibits

rapid initial acceleration
**Effect of rapid initial acceleration**

*Durand and Stone*

\[ \dot{x}_B / x_B \gg \frac{\partial U}{\partial x} \]

for Durand and Stone

Contrast model of Biance et al. (2009)

**Assumes** \[ \dot{x}_B / x_B = \frac{\partial U}{\partial x} \]

Exhibits *very slow* evolution

(note very different time scale cf. Durand and Stone graph)
Rapid motion (*after* initial acceleration) easiest to detect in experiment.

agreement with experiment here

actual start of T1
apparent start of T1
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 $x_B$
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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 $\tau$
- Equilibration is dissipative: decay of chemical potential
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 $\tau^{-1}$.

\[
\frac{dc}{dt} = -s \frac{dL}{ds} c - \frac{(c - c_{eqm})}{\tau}
\]

\[
\left( \text{shear induced film stretch} \right) \quad \left( \text{equilibration with reservoir} \right)
\]

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Dissipation Mechanisms
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)
Hexagonal honeycomb foams
Foams out of mechanical equilibrium
Foams out of physicochemical equilibrium

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

- Film tensions: evolve via ode
- Vertex: constraint eqn $\sum \gamma_i t_i = 0$
- Film midpt: prescribed motion
- Film midpt: fixed
- Film midpt: fixed

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Dissipation Mechanisms
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
\[
\frac{\gamma}{\gamma_{eqm}} = 1 - \bar{\Gamma} \left( \frac{L_{eqm}}{L} - 1 \right)
\]

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

\[ \rightarrow \text{Secular film growth to bursting point?} \]
Consider instead tension model with finite cutoff $\gamma_{min}$ at cmc

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

T1 is more likely if concn ratio $\frac{c_{eq}}{c_{cmc}}$ 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

For Princen, shrinking film length nearly linear in applied strain

![Graph showing deviation from Princenian film length relations](image)

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

\[ 1 - \gamma_{\text{shrinking}} \sim (s - s_{\text{Princen}}) + L_{\text{shrinking}} \]

*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

\[ De \frac{d(c L)}{ds} = L(c_{eqm} - c) \quad \Rightarrow \quad \frac{c}{c_{eqm}} \approx 1 + \frac{De}{L} \left| \frac{dL}{ds} \right| \]

Concn deviation \( c - 1 \) grows from \( O(De) \) to \( O(De^{1/2}) \) but remains small

\[ \rightarrow \text{ Isotherm can be } \text{linearised} \]

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 $s_P$

$$L = \frac{2\sqrt{\bar{\Gamma}} De}{1 + \text{erf}((s - s_P)/\sqrt{\bar{\Gamma}} De)} \exp\left(-\frac{(s - s_P)^2}{\bar{\Gamma} De}\right)$$
Predicted delay in T1

T1 occurs as film length $L$ falls to $\varepsilon$ (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 $\varepsilon$ and then grows
- Mechanical relaxn *followed by* physicochemical relaxn
- Rel. amounts of each equilibration depend on $\bar{\Gamma} \equiv |d\gamma/dc|$
Post-T1 relaxation
Total film energy over all films

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

Before mechanical relaxation

After mechanical relaxation

$O(\varepsilon)$

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

After mechanical relaxation

Before mechanical relaxation

$>> O(\varepsilon)$
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