A Princen hexagonal foam out of physicochemical equilibrium

P. Grassia
CEAS, The Mill, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

B. Embley
Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, 50 Ngamwongwan Road, Jatujak, Bangkok 10900, Thailand

C. Oguey
LPTM, CNRS UMR 8089, University of Cergy-Pontoise, 2 Avenue A. Chauvin, 95302 Cergy-Pontoise, France

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Synopsis
The two-dimensional, regular, hexagonal foam is a common benchmark system for studies of foam rheology under imposed shear. Traditionally, the hexagonal foam has been studied under quasistatic shear deformations. Here, however, nonequilibrium systems are considered. Specifically, the hexagonal foam is assumed to depart from physicochemical equilibrium (surfactant coverage varies and hence surface tension varies between films), but to remain in static mechanical equilibrium (as a consequence, films in the hexagonal foam remain straight, simplifying the geometrical description considerably). Regardless of the mechanism for departing from equilibrium, topological transformations (during which certain films in the hexagonal structure shrink to zero, and bubbles exchange neighbors) tend to be postponed compared to an equilibrium foam. Even when the rate of imposed shear is small, significant departures from physicochemical equilibrium are still observed on the approach to and in the immediate aftermath of a topological transformation. The nature of the relaxation post-topological transformation depends on the variation of film tension with surfactant coverage. It may be almost entirely mechanical (in the case of weakly varying film tension) or almost entirely physicochemical (for a strongly varying film tension). As the imposed shear rate increases, models incorporating weak departures from physicochemical equilibrium prove inadequate to predict the criteria for topological transformation: far-from-equilibrium physicochemical properties must be considered also.

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I. INTRODUCTION
A 2D honeycomb of hexagonal bubbles, with edges of the hexagons representing foam films, has been historically used [Hutzler and Weaire (2011)] as a benchmark model of foam rheology dating back to early work of Princen (1983).

Author to whom correspondence should be addressed; electronic mail: paul.grassia@manchester.ac.uk
When the hexagonal foam is sheared (see Fig. 1), certain edges of the hexagons shrink, while others stretch. Beyond a critical shear strain, the shrinking edges fall to zero length and a so called T1 topological transformation [Weaire and Kermode (1983)] occurs: as a result of this transformation, bubbles exchange neighbors.

The T1 transformation is associated with a relaxation of energy. The Princen model [Princen (1983)] is, however, quasistatic and does not therefore attempt to describe the detailed evolution of this energy relaxation process: Princen’s model exclusively considers foams in static mechanical equilibrium, whereas the T1 is an inherently dynamic phenomenon. In order to describe the evolution of the T1 itself, it is necessary to add an energy dissipation term to the Princen model.

There have been several proposals in the literature regarding the nature of possible viscous dissipation terms. These include intrinsic viscous dissipation in the bulk of the foam films [Kraynik and Hansen (1987); Kraynik (1988)] as well as surface viscosity mechanisms [Durand and Stone (2006); Biance et al. (2009)], and also extrinsic viscous dissipation as the hexagonal foam moves over a substrate [Kern et al. (2004); Cox (2005); Green et al. (2009)].

The choice of which viscous dissipation mechanism is most appropriate depends on the precise nature of which experimental system [Wang et al. (2006)] one is trying to represent by a Princen type model. This could be a bubble raft floating freely on a liquid [Gilbreth et al. (2006)], a bubble monolayer floating on liquid but capped by a covering plate [Katgert et al. (2008)], or a bubble monolayer confined between two plates [Debrégeas et al. (2001); Cantat and Delannay (2003); Drenckhan et al. (2005)].

Regardless of the viscous dissipation mechanism selected, the following generic features apply.

- The onset of the topological transformation is delayed by the presence of viscosity [Green et al. (2009)]. The amount of this delay is determined by a governing dimensionless parameter, the Capillary number, which measures the product of an applied shear rate and a characteristic viscous relaxation time.
- The time interval between T1 transformations is set by the reciprocal of the shear rate. Meanwhile, the duration of an individual T1 transformation is set by the viscous relaxation time. When the Capillary number is small, one sees, therefore, a Princen model punctuated by intermittent [Okuzono and Kawasaki (1995); Gopal and Durian (1995)] non-Princen T1 relaxations.

![FIG. 1. Princen model of a sheared foam. A regular hexagonal honeycomb (top left) is sheared (top right) until a topological transformation occurs (bottom left). The structure relaxes back to a regular honeycomb (bottom right), but the bubbles labeled I and III have now lost contact, while bubbles II and IV have been brought into contact.](image-url)
• When the Capillary number is large, energy is injected into the sheared foam faster than viscosity permits it to relax [Gopal and Durian (1999)]. Considerable film elongation can occur, which may lead to film bursting [Green et al. (2009)].

While, the dynamics of viscous i.e., mechanical dissipation mechanisms in foam have received considerable study, it is sometimes overlooked that there is another way in which a foam can exhibit nontrivial dynamics, i.e., a departure from physicochemical equilibrium.

This can be understood as follows [Buzza et al. (1995)]. Aqueous foams are made using surfactant molecules. If there are spatial nonuniformities in the concentration of surfactant on foam films, then there will be spatial nonuniformities in the surface tension. These nonuniform surface tensions correspond to Marangoni stresses, which can induce fluid motion [Lucassen (1981); Joye et al. (1994); Breward and Howell (2002)]. In this process, the chemical potential of the surfactant is being made to do mechanical work. Moreover, surfactant transport and equilibration processes dissipate a foam’s physicochemical energy, just as conventional viscous processes dissipate its mechanical energy.

Recently, there was an attempt in the literature to add both mechanical viscous dissipation and physicochemical surfactant effects in the Princen hexagonal foam model [Embley and Grassia (2011)]. The resulting model was, however, extremely expensive numerically, and it is worthwhile speculating whether there might be ways that one could elucidate physicochemical dissipation processes in foam within a much simpler modeling framework.

A possible way forward is suggested by comparing the various rates and time scales relevant to the sheared foam. In addition to the imposed shear rate and the characteristic viscous relaxation time (both mentioned above), an additional time scale becomes important, namely the characteristic time for surfactant concentrations on film surfaces to equilibrate.

A key dimensionless parameter is the Deborah number, which is the product of the imposed shear rate and the surfactant equilibration time [Cantat (2011)]: it is the physicochemical analogue of the Capillary number.

It has been proposed that for certain surfactant systems, dependent upon the surfactant chemistry [Denkov et al. (2009)], the surfactant equilibration time may be possibly somewhat larger than a typical viscous relaxation time scale. This offers the intriguing possibility of considering a foam in static mechanical equilibrium (zero Capillary number), but out of physicochemical equilibrium (finite Deborah number).

This very regime has been considered by one study in the literature [Cantat (2011)], albeit not for a 2D Princen hexagonal foam, but rather for a disordered 2D foam. In the interests of simplicity, the films of the bubbles were represented not by circular arcs, as they strictly should be in a static mechanical equilibrium foam, but by straight lines [Cantat (2011)]. This approximation means for instance that the angles at which foam films meet are not well represented in the model, thereby precluding the possibility of asking how those angles might vary with Deborah number.

If one returns to a 2D Princen geometry, however, these objections no longer arise. Pressure differences between bubbles are eliminated on symmetry grounds, so the static mechanical equilibrium foam really should have straight edges. The purpose of this paper therefore is to consider the interplay between imposed shear and surfactant effects on a 2D Princen hexagonal foam.

After setting up the model and governing equations (Sec. II), the influence of the Deborah number on the system behavior will be considered in the extremes of small and large Deborah numbers (Secs. III and IV, respectively). Conclusions are offered in Sec. V.
II. MODEL AND GOVERNING EQUATIONS

The basic model we will employ has been considered already in the literature [Cantat (2011)] so details of the derivation will be only sketched here. More important is to understand how the basic model impacts on the particular hexagonal foam geometry of interest here.

To analyze the hexagonal foam, it is sufficient to consider a unit cell as sketched in Fig. 2. This shows a vertex (labeled \( X_v \)) with three films (to be denoted \( A, B, \) and \( C \)) attached to it.

Figure 2 actually only shows half the length of each film, so that the points \( M_A, M_B, \) and \( M_C \) denote film midpoints. When a given shear strain \( s \) is imposed, \( M_A \) has a known displacement (indeed the shear strain \( s \) is defined as the displacement of \( M_A \) divided by the height of the unit cell), whereas \( M_B \) and \( M_C \) remain fixed in position. Unit tangent vectors \( t_A, t_B, \) and \( t_C \) are defined pointing from \( X_v \) to each of \( M_A, M_B, \) and \( M_C \). Each film has a tension associated with it, denoted \( \gamma_A, \gamma_B, \gamma_C \). Static mechanical equilibrium is then imposed by requiring,

\[
\sum_i \gamma_i t_i = 0,
\]

where the summation index \( i \) runs over \( A, B, \) and \( C \). This is a constraint equation defining the position of \( X_v \).

So far the model is no different from the quasistatic Princen hexagonal foam, except that one is recognizing the possibility that film tensions might be different in the three films. A model for determining film tension is required. Following Embley and Grassia (2011) and Cantat (2011), a linearized Gibbs model is employed relating film tension \( \gamma \) to surface concentration of surfactant \( c \). In suitable dimensionless variables,

\[
\gamma = 1 - \Gamma (c - 1) = 1 + \Gamma - \Gamma c.
\]

In the above, film tensions and surfactant surface concentrations have been made dimensionless based on their values in the unsheared equilibrium hexagonal foam. Meanwhile \( \Gamma \) is a dimensionless Gibbs parameter, which measures the strength of the variation of film tension with respect to surfactant surface concentration. Experimentally [Durand and Stone (2006)], we would expect \( \Gamma \) to be a value of no more than order unity, and it could be substantially less than unity in a system with weak Gibbs elasticity [Biance et al. (2009)].

It is convenient to define a quantity representing the total amount of surfactant on each film. We denote this quantity \( N \) and will call it the surfactant coverage. In our 2D

FIG. 2. Unit cell of the Princen hexagonal foam.
model, like Durand and Stone (2006) and Cantat (2011) but unlike Embley and Grassia (2011), we assume that the surfactant concentration is spatially uniform along a film. Thus by definition when the instantaneous film length is \( L \),
\[
c = N/L.
\] (3)

Lengths \( L \) can be made dimensionless with respect to the edge lengths in the unsheared equilibrium hexagonal foam, so that \( N \) can likewise be made dimensionless. Remember, however, that the unit cell as drawn in Fig. 2 only contains half the length of (and therefore half the surfactant coverage of) each film.

The model can be closed by supplying an evolution equation for surfactant concentration \( c \), or equivalently for \( N \). Following Cantat (2011), we consider that nonconservation of surfactant coverage on films comes about due to some exchange mechanism with a “reservoir,” the “reservoir” being held at a constant surfactant concentration, which would correspond to the (physicochemical) equilibrium surface concentration.

Like Cantat (2011), we are nonspecific regarding the physical chemistry behind this exchange mechanism. It could represent adsorption/desorption between the interior of a film and the surface itself. Alternatively it could represent (for a thin film with relatively insoluble surfactant where the surfactant surface excess dominates that in the film interior) a crude representation of some bulk diffusive and/or fluid mechanical transport mechanism, e.g., transport of surfactant from so called Plateau borders at the edges of films to the interior of films and thence to the surface.

Note that like Embley and Grassia (2011) and Cantat (2011) [and by contrast with Durand and Stone (2006)] we consider only surfactant exchange with a reservoir, and not any direct surfactant exchange between a film and its neighbors. Suppressing surfactant exchange between neighbors, tends to exaggerate surface tension differences between films, and so provides a convenient modeling framework to explore deviations from Princen’s model.

In our model then, the rate of change of surfactant coverage \( N \) due to the (reservoir) exchange mechanism is assumed to be proportional to the film length \( L \), proportional to the difference between the instantaneous surface concentration \( c \) and the “target” equilibrium value, and inversely proportional to some characteristic time scale. Again we are nonspecific about the exact processes governing this time scale and whether it involves kinetic adsorption barriers, or transport of surfactant monomers, or transport of surfactant micelles, or micellar breakdown rates. For practical purposes, one could think of this characteristic time as being, for a sequence of dynamic surface tension measurements [such as those reported in Ran et al. (2011)], the surface age at which the film tension begins to approach the equilibrium film tension value.

In what follows, time \( t \) will be made dimensionless on the characteristic equilibration time scale. The model described above then becomes (in dimensionless form),
\[
\frac{dN}{dt} = -L(c - 1) = -(N - L).
\] (4)

Based on these scalings, the Deborah number \( De \) is now the dimensionless shear rate. Literature suggests that (dimensional) equilibration time scales exhibit wide variation [Golemanov et al. (2008)] but could be up to tens of seconds for selected surfactant systems [Denkov et al. (2009)]. Imposed shear rates of up to about 10 s\(^{-1}\) also seem reasonable in experiment. This suggests Deborah numbers \( De \) could be up to several hundred. However, \( De \) could also be extremely small for a surfactant that equilibrates rapidly
and/or for slow imposed shear. In this paper, therefore, both the extremes of low and high Deborah number will be considered.

To summarize, the model then consists of moving film midpoint $M_A$ at shear rate $De$, solving constraint equation (1) to obtain $X_v$ (and thereby film lengths $L_A, L_B$, and $L_C$) while also tracking the evolution of surfactant coverages $N_A, N_B,$ and $N_C$ via Eq. (4).

It is clear from Figs. 1 and 2 that, under the action of shear, films $A$ and $C$ will grow, while film $B$ will shrink.

A T1 topological event is imposed whenever the length $L_B$ falls below some critical value $\varepsilon$. The quantity $\varepsilon$ is a small parameter, and can be assumed to be a measure of the liquid fraction of the foam.

After the topological event, films are reconnected with those in an adjacent periodic copy of the unit cell as shown in Fig. 3. The new film $B'$ corresponds to the previous film $C$, and it inherits the surfactant coverage $N_C$ of film $C$.

The new film $C'$ is assumed to be created with a surfactant coverage $N_{C'} = \varepsilon$. The lengths of films $A, B',\text{ and } C'$ immediately after the topological transformation are a priori unknown and can only be obtained by solving constraint equation (1) while conserving $N_A, N_{B'},\text{ and } N_{C'}$. Once $L_A, L_{B'},\text{ and } L_{C'}$ have been computed immediately post-T1, shear of film midpoint $M_A$ can be resumed, and the system evolution computed as outlined previously.

III. LOW DEBORAH NUMBER LIMIT

It is clear from Eq. (4) that surfactant coverages tend to equilibrate on order unity time scales. Meanwhile, we know that film midpoint $M_B$ is moved at imposed shear rate $De$. Equation (4) becomes in that case,

$$De \frac{dN}{ds} = -(N - L).$$

---

**FIG. 3.** Reconnection of edges following a T1 event. Newly created film $C'$ has its midpoint $M_{C'}$ at the former point $M_B$. Film $B'$ inherits properties from (a periodic copy of) the former film $C$, so that film midpoint $M_{B'}$ is a periodic copy of the former point $M_C$. 
Throughout this section, we suppose $De \ll 1$. Under these circumstances, we expect $N$ and $L$ to be close, and we should be able to approximate Eq. (5) as,

$$N \approx L - De \frac{dL}{ds}.$$  \hspace{1cm} (6)

For a film such as film $B$, which is shrinking, this says that surfactant coverage $N$ is just slightly above the film length $L$. Provided $De$ is small, we should be able to compute $L$ values to a good approximation via the quasistatic Princen model. In that case, the relation $L$ vs $s$ is given straightforwardly via the solution of a Fermat-Steiner problem [Greenberg and Robetello (1965); Tong and Chua (1995)] and the right hand side of Eq. (6), and hence $N$ can be readily determined.

If Eq. (6) which applies at small $De$, is substituted into our surface tension model,

$$\gamma = 1 - \Gamma \left( \frac{N}{L} - 1 \right),$$  \hspace{1cm} (7)

we obtain

$$\gamma = 1 + \frac{\Gamma De dL}{L} ds,$$  \hspace{1cm} (8)

which can be applied to each of films $A$, $B$, and $C$.

It is interesting to observe that this has the same form as a surface viscosity term such as has been considered by previous authors [Durand and Stone (2006); Biance et al. (2009); Barry (2010)]. Thus weak Gibbs elasticity manifests itself in the same way as surface viscosity, despite the fact that surface viscosity has not been formally included anywhere in our model.

To summarize, Eq. (8) with $L$ given by Princen’s quasistatic formula represents a good approximation to the film tension $\gamma$ in a foam model incorporating surfactant transport effects at low $De$. The question is whether any circumstances arise in which it is not permitted to use Eq. (8) even though $De$ is small.

An obvious case is on the approach to a T1. In Princen’s model, assuming an arbitrarily dry foam, the length $L_B$ of film $B$ theoretically falls to zero as $s$ approaches a strain that we call the Princen yield strain $s_P \equiv \sqrt{3}/3$.

Under those circumstances the changes in film tension predicted on the right hand side of Eq. (8) must begin to influence the film lengths, which must then deviate from the Fermat-Steiner Princen predictions. When and how those changes come about and the effects produced by them are considered in Subsections III A–III F.

**A. System behavior on the approach to the Princen yield strain**

Figure 4 shows the calculated length of the shrinking film $B$ as a function of applied strain for Deborah numbers either $De = 1/256$ or $De = 1/64$ and for $\Gamma = 1$.

Clearly for sufficiently small film lengths, discrepancies are seen from the Fermat-Steiner Princen predictions: the decay of $L_B$ at finite $De$ is arrested compared to Princen’s $De \rightarrow 0$ case.

This leads to a delay in the onset of T1. For a fixed value of the liquid fraction parameter $\varepsilon$, the amount of the delay is a function of $De$ and $\Gamma$. Empirically (see Fig. 5), it seems to exhibit a power law behavior (with exponent 0.66) in the product $\Gamma De$.

In the low Deborah number limit, film tensions in films $A$ and $C$ should remain near unity, apart from small perturbations described by Eq. (8), with $L_A$ and/or $L_C$ vs imposed
strain $s$ given by Princen relations. On the approach to $T_1$, however, film $B$ should see more significant changes in its surfactant concentration and therefore its film tension. This is because it undergoes orders of magnitude of decrease in its length, from unit length initially to length $\varepsilon$ at $T_1$. Data for surfactant concentration vs imposed strain (see Fig. 6) reveal that surfactant concentration deviates from unity by only $O(De)$ amounts far from $T_1$, but by substantially larger amounts close to $T_1$.

Explanations for the results in Figs. 4–6 are given in Subsections III B–III D, employing a perturbation analysis approach.

B. Perturbation analysis on approach to the Princen yield strain

Our perturbation analysis proceeds as follows.

We begin by computing the net pull on films $A$ and $C$, taken (since $\gamma_A \approx \gamma_C \approx 1$) as the magnitude of the vector sum of the corresponding tangent vectors $|t_A + t_C|$. We shall denote this magnitude by $\gamma_{AC}$.

This magnitude depends on the angle enclosed between the vectors $t_A$ and $t_C$. Increasing the angle causes the net pull $\gamma_{AC}$ to decrease.

Perturbing about the Princen yield strain $s_P$, there are two effects upon $\gamma_{AC}$ of which we need to take account.

The first (see Fig. 7) is the effect of a small but finite film length $L_B$. This opens up the enclosed angle and reduces $\gamma_{AC}$. The second is the effect of moving the film midpoint...
M. This swivels the enclosed angle open (as in Fig. 7) if imposed strain $s > s_P$ (reducing $\gamma_{AC}$), but swivels it shut if $s < s_P$ (increasing $\gamma_{AC}$).

The net result is

$$\gamma_{AC} = 1 - \frac{3\sqrt{3}}{8}(s - s_P) - \frac{\sqrt{3}}{2}L_B.$$  \hspace{1cm} (9)

Static mechanical equilibrium requires that $\gamma_{AC} = \gamma_B$ and hence

$$\frac{3\sqrt{3}}{8}(s - s_P) + \frac{\sqrt{3}}{2}L_B + (\gamma_B - 1) = 0.$$  \hspace{1cm} (10)

An interpretation of this equation is that $L_B$ approximates to $(3/4)(s_P - s)$ (which is Princen’s result on the approach to T1), but with a small perturbative increase in film length due to the fact that $\gamma_B < 1$. A film with tension slightly below unity is slightly less costly energetically than one with unit tension, and so can sustain a slightly higher length.

By Eqs. (8) and (10) a significant deviation from the Princen film length relations can occur as soon as $\left|\frac{(s_P - \gamma_B - 1)}{L_B}\right|=O(1)$.

Remember that our trigger for inducing the T1 is that $L_B$ should fall as low as the foam liquid fraction parameter $\varepsilon$.

If $O((\Gamma De)^{1/2}) \ll \varepsilon \ll 1$ the strain to T1, denoted $s_{T1}$, can be computed entirely via Princen’s model,

$$s_{T1} = s_P - \frac{4}{3}\varepsilon.$$  \hspace{1cm} (11)

FIG. 6. Deviation from equilibrium of the surfactant concentration for film $B$ vs imposed shear strain computed for $De = 1/64$ and $De = 1/256$ up to the point of T1. Data have been collapsed away from the T1 by normalizing by $De$. Other parameters are $\Gamma = 1$ and $\varepsilon = 1/128$. The curve labeled “via Princen” utilizes Eq. (8) but assuming the film length vs imposed strain relations derived by Princen.

$M_A$. This swivels the enclosed angle open (as in Fig. 7) if imposed strain $s > s_P$ (reducing $\gamma_{AC}$), but swivels it shut if $s < s_P$ (increasing $\gamma_{AC}$).

FIG. 7. Net pull from films $A$ and $C$ in the neighborhood of a T1 depends on the angle between films $A$ and $C$, and hence on the magnitude of the vector sum of the tangents $|t_A + t_C|$. This is influenced by the finite length of film $B$ and by the swivel of film midpoint $M_A$. 

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leading to the notion that a finite liquid fraction preempts the T1 slightly.

On the other hand, if \( O((\Gamma De)^{1/2}) \geq \varepsilon \), non-Princen film length relations \((L_B \text{ vs } s)\) need to be computed, in order to obtain \(s_{T1}\). This will be done in two separate cases: for the case \( De \ll 1 \) with \( \Gamma \) being order unity (Subsection III C) and for the case \( \Gamma \ll De \ll 1 \) (Subsection III D).

C. The case \( De \ll 1 \) and \( \Gamma = O(1) \)

Our aim here is to use the perturbation analysis of Sec. III B to deduce an analytic formula for surfactant coverage \(N_B\) on film \(B\) on the approach to the Princen yield strain \(s_p\). Subsequently the analytical formula will be used to probe imposed strains in excess of the Princen yield strain, a regime that Princen’s original analysis could not access. The results derived enable us to determine the delay to T1 as a function of the parameters \(\Gamma, De,\) and \(\varepsilon\).

We proceed as follows. From Eqs. (7) and (10), we deduce that

\[
\frac{N_B}{L_B} = 1 + \frac{(1 - \gamma_B)}{\Gamma} = 1 + \frac{1}{\Gamma} \left( \frac{3\sqrt{3}}{8} (s - s_P) \right) + \frac{1}{\Gamma} \left( \frac{\sqrt{3}}{2} L_B \right).
\]  

Suppose in the first instance that \(s < s_P\). As was stated above, in the regime where \(L_B\) values can differ significantly from Princen’s result \((3/4)(s_P - s)\), we have \(L_B \leq O((\Gamma De)^{1/2})\) and also \(s_P - s \leq O((\Gamma De)^{1/2})\).

Under our current assumptions with \(De \ll 1\) and \(\Gamma = O(1)\), it is clear that \(N_B/L_B\) differs from unity by at most an \(O(De^{1/2}/\Gamma^{1/2})\) amount. In that case, it is also permitted to replace the term \(L_B\) on the right hand side of Eq. (12) by \(N_B\). Moreover, if we write the surfactant evolution Eq. (5) as,

\[ De \frac{dN_B}{ds} = -\left( \frac{N_B}{L_B} - 1 \right) L_B, \]  

substitute from Eq. (12) and again replace the final factor \(L_B\) by \(N_B\), we obtain

\[
De \frac{dN_B}{ds} = -\frac{1}{\Gamma} \left( \frac{3\sqrt{3}}{8} (s - s_P) \right) N_B - \frac{1}{2} \frac{\sqrt{3}}{2} N_B^2.
\]  

The solution is

\[
N_B = \frac{3^{1/4}}{\sqrt{\pi}} \sqrt{\Gamma De} \left( \text{erf} \left( \frac{3^{1/4} (s - s_P)}{4\sqrt{\Gamma De}} \right) + 1 \right)^{-1} \exp \left( -\frac{3\sqrt{3}}{16\Gamma De} (s - s_P)^2 \right).
\]  

Remember that \(N_B\) and \(L_B\) are close, so Eq. (15) can be viewed also as a prediction for surfactant coverage.

This formula is plotted in Fig. 8 compared to a numerical solution of equations (1) and (5), for the values \(\Gamma = 1\) and \(De = 1/64\). Agreement is good considering that Eq. (15) is an asymptotic formula that is valid only in the limit of small \((\Gamma De)^{1/2}\) values: this permits us to use Eq. (9) (from which Eq. (15) has been derived) in the neighborhood of \(s = s_P\).

This formula (15) correctly approaches Princen’s result \(N_B \approx L_B \approx (3/4)(s_P - s)\) in the limit of \(s_P - s \gg O((\Gamma De)^{1/2})\).

It is clear, both from Fig. 8 and from Eq. (15), that \(N_B\) and hence \(L_B\) remain at finite values as \(s \to s_P\) (unlike the Princen case for which \(L_B\) would approach zero in this limit).
If the predicted film length for \( s \rightarrow s_P \) exceeds the liquid fraction parameter \( \varepsilon \), it is possible to contemplate \( s \) values all the way up to and even in excess of \( s_P \) in Eq. (15). The asymptotic behavior of Eq. (15) in the separate limits \( j s/C_0 \) and \( s/C_28 \) will therefore be considered below.

1. The limit \( |s - s_P| \ll O((\Gamma De)^{1/2}) \)

For \( |s - s_P| \ll O((\Gamma De)^{1/2}) \), Eq. (15) approaches

\[
N_B = 3^{1/4} \sqrt{\Gamma De} \left( 1 + \frac{3^{3/4}}{2\sqrt{\pi}} \frac{(s - s_P)}{\sqrt{\Gamma De}} \right)^{-1}.
\]

Expressing this in terms of time \( t \) instead of strain \( s \) (with a Princen yield time defined as \( t_P \equiv s_P/De \)),

\[
N_B = 3^{1/4} \sqrt{\Gamma De} \left( 1 + \frac{3^{3/4}}{2\sqrt{\pi}} \frac{De}{\Gamma} \sqrt{t - t_P} \right)^{-1}.
\]

A physical interpretation can be attached to this solution as follows. Consider a hexagonal foam which is sheared to within a strain \( \delta s \) of the Princen yield strain \( s_P \), and then is held there indefinitely. Assuming \( \delta s \ll 1 \), the system will equilibrate to a state with \( N_B = L_B = (3/4)\delta s \). Suppose subsequently at some time (again denoted \( t_P \)) the imposed strain is instantaneously changed exactly to strain \( s_P \), and the length of film \( B \) is permitted to relax. The relaxation will follow,

\[
N_B = \frac{3}{4} \delta s \left( 1 + \frac{3\sqrt{3}}{8} \frac{\delta s}{\Gamma} (t - t_P) \right)^{-1}.
\]

This clearly agrees with Eq. (17) provided we make the association,

\[
\delta s \leftrightarrow 4(\Gamma De)^{1/2}/(3^{3/4}\sqrt{\pi}).
\]

The reason such a solution becomes relevant even in a continuously sheared foam can be seen by considering the balance of terms in Eq. (10).
For \( s_P - s \gg ((\Gamma De)^{1/2}) \), the dominant balance is between the first two terms in the equation meaning that increases in imposed strain \( s \) drive shrinkage in film length \( L_B \).

However as \( s_P - s \) falls, surfactant accumulation in film \( B \) starts to resist further shrinkage in \( L_B \) even though \( s_P - s \) continues to fall. Eventually \( s \) attains the value \( s_P \), yet a small amount of surfactant remains in the (continuously sheared) film: the dominant balance is now between the final two terms in Eq. (10).

Under those circumstances Eq. (14) indicates the rate of change of surfactant coverage is proportional to the square of the instantaneous coverage. The surfactant coverage exhibits a slow power law decay, both because the amount of surfactant in the film is low (\( N_B \) is small), and because surfactant is nearly at equilibrium (\( N_B \) and \( L_B \) are close).

Figure 8 compares Eq. (16) with Eq. (15). Clearly Eq. (16), with its extremely slow power law decay, only matches the more general formula equation (15) for a very brief interval of imposed strains in the neighborhood of \( s_P \). What happens beyond that interval is considered next.

2. The limit \( s - s_P \gg O((\Gamma De)^{1/2}) \)

Beyond the Princen yield strain, as \( s - s_P \) grows, surfactant coverages \( N_B \) (and hence film lengths \( L_B \)) as determined by Eq. (15) continue to decrease. The dominant balance in Eq. (10) is now between the first and third terms. This suggests a new physical interpretation of the static mechanical equilibrium condition Eq. (10).

Recall that the conventional interpretation (following Princen) is that the film length \( L_B \) depends on the extent to which imposed strain \( s \) falls short of the Princen yield strain \( s_P \), with a perturbation due to non-Princen variable film tension.

However, this conventional interpretation ceases to be useful if the T1 is delayed beyond the Princen yield strain. In the case \( s > s_P \), it is not meaningful to perturb about Princen’s system, because Princen’s system has already undergone a T1.

Instead the physical content of Eq. (10) is that the net pull \( \gamma_{AC} \) of films \( A \) and \( C \) weakens as the system swivels past the Princen yield strain, and this net pull must be matched to that of film \( B \), i.e. matched to \( \gamma_B \). Via Eq. (7), the amount of additional swivel \( s - s_P \) therefore defines, not the film length \( L_B \), but rather the film surfactant concentration \( N_B/L_B \). This relation between \( N_B \) and \( L_B \), coupled to Eq. (5), is then sufficient to determine how \( N_B \) evolves. The relation between \( s - s_P \) and \( N_B/L_B \) is only very slightly perturbed by the presence of finite film length \( L_B \) (to the extent that the second term in Eq. (10) is now much smaller than either the first or third term).

In the limit as \( s - s_P \gg (\Gamma De)^{1/2} \), Eq. (15) reduces to

\[
N_B = \left( \frac{3^{1/4} \sqrt{\Gamma De}}{2\sqrt{\pi}} \right) \exp \left( -\frac{3\sqrt{3}}{16\Gamma De} (s - s_P)^2 \right). \tag{20}
\]

This is also plotted in Fig. 8, and Eq. (15) is seen to approach closely to it.

Expressing in terms of time \( t \) rather than strain \( s \) yields

\[
N_B = \left( \frac{3^{1/4} \sqrt{\Gamma De}}{2\sqrt{\pi}} \right) \exp \left( -\frac{3\sqrt{3}De}{16\Gamma} (t - t_P)^2 \right). \tag{21}
\]

Note that Eqs. (20) and (21) describe a Gaussian decay, rather than a simple exponential. Note that had the ratio \( N_B/L_B \) been held at a constant value (different from unity), Eq. (4) would have predicted instead an exponential decay, with the decay rate proportional to
the amount that $N_B/L_B$ differs from unity. Specifically consider the case where one slowly shears a hexagonal foam to within a strain $\delta s$ (where $\delta s \ll 1$) of the Princen yield strain, holds it there for an arbitrarily long time until it equilibrates at which point $N_B = L_B = (3/4)\delta s$, and then imposes (at some time denoted $t_P$) an additional instantaneous strain (large compared to $\delta s$ but still small compared to unity) to take the system to a final strain $s_f$ and hold it there. The solution for $N_B$ is

$$N_B = \frac{3}{4} \delta s \exp\left( -\frac{3\sqrt{3}}{8} \frac{(s_f - s_P)(t - t_P)}{\Gamma} \right).$$

(22)

If one makes the association $\delta s \rightarrow 2(\Gamma De)^{1/2}/(3^{3/4}\sqrt{\pi})$ this becomes

$$N_B = \left( \frac{3^{1/4}\sqrt{\Gamma De}}{2\sqrt{\pi}} \right) \exp\left( -\frac{3\sqrt{3}}{8} \frac{(s_f - s_P)(t - t_P)}{\Gamma} \right),$$

(23)

which clearly agrees with Eq. (21) at time $t_P$.

Initially the Gaussian (20) decays more slowly than the exponential (23), but eventually starts to decay more quickly. Given that decay rates are associated with the amount that $N_B/L_B$ deviates from unity, this is a manifestation of $N_B/L_B$ in the Gaussian solution deviating increasingly from unity as $t - t_P$ (or equivalently $s - s_P$) grows.

Using the Gaussian solution, we can predict the strain to T1 for a given liquid fraction $\epsilon$,

$$s_{T1} = s_P + \left( \log\left( \frac{3^{1/4}\sqrt{\Gamma De}}{2\sqrt{\pi}e} \right) \right)^{1/2} \frac{4(\Gamma De)^{1/2}}{3^{3/4}}.$$  

(24)

This provides a formula for the strain to T1 which should be valid in the regime $\epsilon \ll (\Gamma De)^{1/2} \ll 1$. The formula contains no free fitting parameters. Moreover for a fixed liquid fraction parameter $\epsilon$, the delay in strain to T1 brought about by finite $\Gamma De$ is obtained via the difference between Eqs. (24) and (11),

$$s_{T1} - s_{T1,\Gamma De\rightarrow 0} = \frac{4}{3} \epsilon + \left( \log\left( \frac{3^{1/4}\sqrt{\Gamma De}}{2\sqrt{\pi}e} \right) \right)^{1/2} \frac{4(\Gamma De)^{1/2}}{3^{3/4}}.$$  

(25)

Figure 9 shows the numerically computed delays in strain to T1 as a function of $\Gamma De$. These compare well with the predictions of Eq. (25) which roughly shows a square root
dependence in $\Gamma De$, but with a logarithmic correction factor, explaining the slightly higher power observed empirically in Fig. 5.

Observe also that Eq. (24) breaks down as $\Gamma De$ becomes too large (see also Fig. 9), as all the derivations leading up to it (e.g., Eq. (9)), rely on $sT_1$ being close to the Princen yield strain $s_p$.

Finally it is worth noting that Eqs. (12) and (24) also enable us to interrogate the deviation from equilibrium in the surfactant concentration $c_B$ at the point of $T_1$ (cf. Fig. 6). This should be $(3\sqrt{3}/8)(sT_1 - s_p)/\Gamma$, roughly an $O((De/\Gamma)^{1/2})$ value, in the present limit $\varepsilon \ll (\Gamma De)^{1/2}$.

D. The case $\Gamma \ll De \ll 1$

Equation (6) was derived from Eq. (5) as a perturbation expression for surfactant coverage $N$ under the assumption that $L$ vs $s$ followed the Princen film length relations, and also under the supposition that $N \approx L$.

However, it is possible for Eq. (6) to remain valid even if the ratio $N/L$ is very different from unity, provided the difference $N - L$ is (roughly) independent of strain $s$.

Such a situation arises for film $B$ in the case $\Gamma \ll De \ll 1$, i.e., the Gibbs elasticity is assumed to be exceedingly weak.

Under these circumstances, we can use the Princen film length relation $L_B \approx (3/4)(s_p - s)$ to solve Eq. (5) to obtain

$$N_B = L_B + \frac{3}{4}De. \quad (26)$$

It is clear that $N_B/L_B$ becomes much larger than unity as soon as $L_B = O(De)$, ensuring that

$$\gamma_B \approx 1 - \frac{3 \Gamma De}{4 L_B}. \quad (27)$$

Moreover, this occurs long before the Princen film length relation ($L_B$ vs $s$) breaks down which requires $L_B = O((\Gamma De)^{1/2})$.

However, as soon as $N_B/L_B \gg 1$, Eq. (5) becomes insensitive to the value of $L_B$, and reduces to an exponential decay of $N_B$ with respect to applied strain, such that $N_B$ decays on a characteristic strain scale $O(De)$. This characteristic scale turns out, however, to be much greater than the characteristic scale for the decay of $L_B$ once Eq. (10) enters the non-Princen regime for film lengths. Thus provided $|s - s_p| \ll De$, the surfactant coverage $N_B$ can be considered fixed at the value $(3/4)De$, while Eqs. (10) and (27) reduce to a quadratic equation in $L_B$ of which the solution is

$$L_B = -\frac{3}{8}(s - s_p) + \left(\frac{3}{8}(s - s_p)\right)^2 + \frac{\sqrt{3}}{2} \frac{\Gamma De}{\Gamma De}^{1/2}, \quad (28)$$

approximating to (for $s - s_p \gg (\Gamma De)^{1/2}$),

$$L_B \approx \frac{2}{\sqrt{3}} \frac{\Gamma De}{(s - s_p)}. \quad (29)$$

Provided $(\Gamma De)^{1/2} \ll s - s_p \ll De$ Eqs. (27) and (29) give sensible predictions for $\gamma_B$ and $L_B$, respectively.
Meanwhile the strain to T1 satisfies [using Eqs. (10) and (27)],

$$s_{T1} = s_P - \frac{4}{3} \varepsilon + \frac{2}{\sqrt{3}} \frac{\Gamma De}{\varepsilon}. \quad (30)$$

Whether $s_{T1}$ is less or greater than $s_P$ depends on whether $\varepsilon > (3^{1/4}/\sqrt{2})(\Gamma De)^{1/2}$ or $\varepsilon < (3^{1/4}/\sqrt{2})(\Gamma De)^{1/2}$.

E. System behavior following a T1

To date we have considered only how surfactant effects delay the onset of T1 compared to the Princen model. Deviations from the Princen model are also expected immediately after a T1: the state of a foam immediately after a T1 is inherently dynamic and cannot be described by any static mechanical equilibrium balance.

The situation we consider immediately after a T1 is sketched in Fig. 10 still assuming the limit of small $De$. The two films labeled $A$ and $B'$ both have surfactant coverages $\sqrt{3}$.

Meanwhile the newly created film $C'$ is assumed to have a surfactant coverage $\varepsilon$.

As alluded to above, the state in which film $C'$ has a length exactly equal to $\varepsilon$, is not a static mechanical equilibrium state. A mechanical relaxation must occur, lengthening film $C'$ (thereby raising its film tension) and shortening films $A$ and $B'$ (thereby lowering their film tensions).

This extremely rapid mechanical relaxation cannot be resolved by the present model as defined in Sec. II. A generalization of the model would be required, e.g., incorporating a surface viscosity term as in Durand and Stone (2006) and Bianco et al. (2009), but the details of this will not be considered here.

Once the mechanical relaxation is complete, the system must undergo an additional physicochemical relaxation, which tries to restore the film tensions to equilibrium: this can be captured by the model in Sec. II. The vertex location shifts as the film coverages evolve, producing evolution of the film lengths.

An interesting question is how much of the film length relaxation is mechanical vs how much is physicochemical. It turns out that if $\Gamma$ is larger than $\sqrt{3} - 1$, relaxation is

![FIG. 10. The state immediately after a T1, both pre- and post-mechanical relaxation.](image-url)
primarily physicochemical. On the other hand, if $\Gamma$ is smaller than $\sqrt{3} - 1$, significant mechanical relaxation occurs. The explanation is as follows.

In a state in which film $C'$ is short (with a length somewhere in the neighborhood of $\varepsilon$), the net pull of films $A$ and $B'$ is $\sqrt{3}$. In that case, static mechanical equilibrium is attained when

$$L_{C'} = \varepsilon \left( 1 - \frac{\sqrt{3} - 1}{\Gamma} \right)^{-1}. \quad (31)$$

Clearly $L_{C'}$ is an $O(\varepsilon)$ quantity as long as $\Gamma > \sqrt{3} - 1$.

For $\Gamma < \sqrt{3} - 1$, it is not possible to achieve static mechanical equilibrium for any $L_{C'}$ in the neighborhood of $\varepsilon$. Instead film $C'$ will grow to a length many times $\varepsilon$ where its surface tension will saturate at the value of $1 + \Gamma$. The vertex $X_v$ must find a position such that the net pull of films $A$ and $B'$ balances $1 + \Gamma$: This then is the static mechanical equilibrium state post-$T_1$.

The length of film $C'$ in this state as a function of $\Gamma$ is plotted in Fig. 11.

Note that the critical value $\Gamma = \sqrt{3} - 1$ at which the length of film $C'$ post-mechanical relaxation switches between $O(\varepsilon)$ values and values greatly in excess of $\varepsilon$, is sensitive to our assumption (see Sec. II) that surfactant exchanges with a reservoir and not with neighboring films.

In an alternative model which permits surfactant exchange with neighboring films (Durand and Stone (2006)), film $C'$ would be less “stiff”: its tension would exhibit comparatively modest increases as the film length grows, and static mechanical equilibrium states with film lengths many times $\varepsilon$ would be the norm for any realistic value of $\Gamma$.

Regardless of where the static mechanical equilibrium state is situated, once it is attained, physicochemical processes now gradually equilibrate all film lengths, $L_A$, $L_{B'}$, and $L_{C'}$ towards unity.

Computations of this physicochemical relaxation for $De = 1/256$ and various $\Gamma$ are shown in Fig. 12: relaxation seems to occur on the order of about 1–10 time units.

If $\Gamma > \sqrt{3} - 1$ the relaxation is noticeably slower than when $\Gamma < \sqrt{3} - 1$. In the former case, surfactant coverages $N$ change slowly for films $A$ and $B'$ because $N$ and $L$ are nearly the same for each film (implying that the right hand side of Eq. (4) is small). Likewise $N$ changes slowly for film $C'$ because $N$ and $L$ are both small (again ensuring the right hand side of Eq. (4) is small), even though $N/L$ is no longer near unity. Remember,
however, despite this comparatively slow physicochemical equilibration on the order of 10 time units, this still corresponds to a very small interval of imposed strain if $De \ll 1$.

In theory, in the limit $De \to 0$, the total film length should relax back to three (i.e., unit length per film) which is Princen’s unsheared state. In practice, since $De$ is finite in these computations, and the physicochemical relaxation occurs over a small but finite interval of imposed strain, the location of film midpoint $M_A$ displaces a little during the physicochemical relaxation, and this theoretical minimum film length is never quite achieved.

### F. Shear stress

Figures 4, 8, 11, and 12 all showed data for film lengths, whereas Fig. 6 showed film surfactant concentration data (from which a film tension can be deduced). Rheology of course concerns itself primarily with stresses, which, in this particular system of a hexagonal foam, depend on both film length and film tension data.

Specifically, shear stress (denoted $\sigma_{xy}$) can be determined [Cantat (2011)] by the formula of Batchelor [Batchelor (1970, 1971)],

$$\sigma_{xy} = e_x e_y : \sum_i \gamma_i L_i t_i / (2A_{\text{cell}}),$$

where $e_x$ and $e_y$ are Cartesian unit vectors, where the summation runs over the three films $A$, $B$, and $C$, and where $A_{\text{cell}}$ is the area of the unit cell (specifically the area of the
enclosing quadrilateral in Fig. 2). The factor 2 in the denominator here recognizes that only half the length of each film is contained in the unit cell.

Stress-strain relationships for a Princen hexagonal foam, and for a hexagonal foam driven out of physicochemical equilibrium (values of $De = 1/64$ and $De = 1/256$) are shown in Fig. 13: all data have been nondimensionalized here. Parameter values of $\Gamma = 1$ and $\Gamma = 1/4$ are considered for $De = 1/64$, whereas just $\Gamma = 1$ is considered for $De = 1/256$. Values of strain $s$ are considered varying from 0 to $3s_p$.

In all cases shown, significant departures from the Princen results can be observed for finite $De$ and $\Gamma$, especially in the neighborhood of a topological transformation. Indeed the delay in topological transformation due to departures from physicochemical equilibrium manifests itself as a stress “overshoot” compared to the Princen case.

The size of the overshoot seems to depend primarily on the value of the product $\Gamma De$ rather than on $\Gamma$ and $De$ individually. This is evident because the curve for the case $\Gamma = 1$ and $De = 1/256$ nearly coincides with (and is difficult to distinguish from) that for $De = 1/64$ and $\Gamma = 1/4$.

The size of the stress overshoot relative to Princen in the case $\Gamma De = 1/64$ seems to be a little more than twice the size of the overshoot for the case $\Gamma De = 1/256$. This is entirely consistent with the stress overshoot scaling proportionally to the delay in strain to $T_1$ [as predicted by Eq. (25)].

Immediately upon $T_1$, a jump in the stress instantaneously occurs: this is associated with mechanical dissipation (i.e., viscous effects), the detailed evolution of which is unresolved in the present model.

For the cases with $\Gamma = 1$ (regardless of whether $De = 1/256$ or $De = 1/64$), this stress jump is very small, and manifests itself as a small gap in the curves in Fig. 13. For the case with $\Gamma = 1/4$, the instantaneous jump in stress is more significant. This behavior for stress is consistent with the results reported for mechanical relaxation of film lengths in Sec. III E, Figs. 11 and 12.

After this (instantaneous) mechanical relaxation, a physicochemical stress relaxation occurs, over a small, but finite strain.

As in Fig. 12, the physicochemical relaxation occurs over $O(1)$ time scales, and hence over $O(De)$ strain intervals: in Fig. 13 therefore, the relaxation for $De = 1/256$ occupies a smaller strain interval than that for $De = 1/64$. Moreover, for a given $De$, the physicochemical relaxation time (and hence the associated strain interval in Fig. 13) is sensitive to $\Gamma$, for reasons we have already discussed in Sec. III E.

Although the Princen hexagonal foam relaxes back to zero stress after each and every topological transformation, the nonequilibrium systems with finite $De$ and $\Gamma$ do not do

![FIG. 13. Stress (in dimensionless form) vs imposed strain for a Princen hexagonal foam, and also for a hexagonal foam driven out of physicochemical equilibrium with various values of $De$ and $\Gamma$.](image)
so. In these latter systems, the imposed strain required to invoke a T1 is already greater than the Princen yield strain, while yet more imposed strain is accumulated during physicochemical relaxation post-T1.

Upon completion of the physicochemical relaxation phase, it is evident from Fig. 13, that stress returns to a value very close to that corresponding to the Princen system at the same imposed strain. However, in the case $De = 1/64$ and $\Gamma = 1$ for instance, this is already so far in excess of the Princen yield strain, that the corresponding stress is already roughly half the yield stress for the Princen system.

Because the nonequilibrium systems already have, after the first T1, an imposed strain in excess of the Princen yield strain $s_P$, as well as a stress that never relaxes back completely to zero, the second T1 follows just $s_P$ strain units after the first. In other words, the nonequilibrium systems do not “fall any farther behind” the Princen system after the first T1, but exhibit instead (see Fig. 13) a periodic behavior with period $s_P$.

IV. HIGH DEBORAH NUMBER LIMIT

To date we have considered the low Deborah number limit, in which the system follows Princen type behavior, except in the neighborhood of a T1.

In the high Deborah number limit, we expect to see large deviations from the Princen case.

On the scale of the applied strain, film coverages are now conserved, and Eq. (7) reduces to

$$\gamma = 1 - \Gamma \left( \frac{1}{L} - 1 \right).$$

The net effect is a strong suppression of T1 transformations: Any initial decreases in film length for a film that shrinks under the influence of imposed shear cause a decrease in film tension, which then removes the driver for further decreases in film length.

Indeed the only scenario under which Eq. (33) permits T1 transformations is when the Gibbs parameter $\Gamma$ is very small, in fact smaller than the liquid fraction parameter $\epsilon$. We consider this case first of all.

A. Case $\Gamma < \epsilon$

Although topological transformations can occur whenever $\Gamma < \epsilon$, it is easiest to consider first of all the case $\Gamma \ll \epsilon$.

In that case, not only does a topological transformation occur, it occurs in the neighborhood of the Princen yield strain $s_P$.

Remarkably Eq. (9) now applies. The derivation of Eq. (9) relied on the fact that the film tensions in films $A$ and $C$ were near unity, so that the net pull of films $A$ and $C$ could be computed just in terms of the angle enclosed by the film tangents $t_A$ and $t_C$. In Sec. III B, the tensions in films $A$ and $C$ were near unity solely because $De$ was small. Here, however, the tensions in films $A$ and $C$ are near unity because $\Gamma$ is small (even though $De$ is now large).

Section III D solved for film length $L_B$ as a function of applied strain in the particular case where the surfactant coverage was fixed at the value $(3/4)De$. Exactly the same considerations apply here except that the surfactant coverage of film $B$ is now unity. The strain to T1 becomes analogous to Eq. (30),
Equation (34) is only valid when $\Gamma \ll \varepsilon$. As $\Gamma/\varepsilon$ grows toward unity, $s_{T1}$ starts to differ significantly from $s_P$. In that case Eq. (9), from which Eq. (34) was derived, loses validity.

It is still, however, possible to compute the net pull $\gamma_{AC}$ of films A and C numerically in terms of imposed strain $s$. Moreover, static mechanical equilibrium requires that $\gamma_{AC}$ balances the tension in film B, which at the point of T1, is to leading order,

$$\gamma_{B,T1} \approx 1 - \frac{\Gamma}{\varepsilon}. \tag{35}$$

Numerical predictions of strain to T1 employing this balance are shown in Fig. 14. It is possible moreover to demonstrate that as $\Gamma \to \varepsilon$,

$$s_{T1} \approx \left(1 - \frac{\Gamma}{\varepsilon}\right)^{-1}, \tag{36}$$

which is also plotted in Fig. 14. It is clear from Eq. (36) that topological transformation is delayed up to increasingly high imposed strains as $\Gamma$ approaches $\varepsilon$, leading to high film elongation and possible film bursting.

**B. Case $\Gamma > \varepsilon$**

To date we have considered the case of high Deborah number when $\Gamma < \varepsilon$.

For high Deborah number, topological transformations are suppressed whenever $\Gamma \geq \varepsilon$. The reason for this can be seen immediately by consulting Eq. (35). Our linear film tension model predicts a negative tension in film B at T1 which is unphysical. Even switching from the linearized film tension model of Eq. (2) to a standard Gibbs isotherm [Durand and Stone (2006)], whereby variations in film tension $\gamma$ depend on variations of the logarithm of surfactant surface concentration $c$ (rather than just on variations of $c$ itself), does not resolve this problem.

To obtain a physically sensible model, it is necessary to replace the linearized Gibbs film tension model Eq. (2) by a nonlinear model which saturates at a finite positive tension even as surfactant surface concentration $c$ becomes large: this is done in the Subsection IV C.

![FIG. 14. Strain to T1 as a function of $\Gamma/\varepsilon$ in the large Deborah number limit.](image-url)
C. Nonlinear film tension models

Literature [Marmottant et al. (2005)] suggests that, in the limit of high surfactant surface concentration, film tension saturates at a value which, for certain surfactant types, could be as low as 0.15 times the surfactant-free film tension. This saturation of the tension has, moreover, been associated with buckling of the surface.

It has been previously proposed in the literature [Marmottant et al. (2005)] to use a linear model like Eq. (2) down to the saturation film tension, and a constant film tension thereafter. We select instead the following nonlinear model which is just a smoothed out version of the above proposal,

\[ \gamma = \gamma_{\text{max}} - \frac{cC_0}{1 + cC_0} \gamma_{\text{max}} (1 - \hat{\gamma}), \]  

where \( C_0 \) and \( \hat{\gamma} \) are model parameters, and where

\[ \gamma_{\text{max}} = \frac{(1 + C_0)}{(1 + \hat{\gamma}C_0)}. \]

We suppose that \( C_0 > 0 \) and \( 0 < \hat{\gamma} < 1 \). Then it is evident that (see Fig. 15) as \( c \) increases, \( \gamma \) decreases smoothly from \( \gamma = \gamma_{\text{max}} \) as \( c \to 0 \), to \( \gamma = 1 \) when \( c = 1 \), to \( \gamma = \gamma_{\text{min}} \equiv \hat{\gamma}\gamma_{\text{max}} \) as \( c \to \infty \).

The film tension model equation (37) predicts (see Fig. 15) a roughly linear decrease in tension up to \( c \ll C_0^{-1} \) [so that Eq. (2) is regained in that limit] but a barely changing tension for \( c \gg C_0^{-1} \). Thus the size of \( C_0 \) determines where the physicochemical equilibrium state \( c = 1 \) sits on the film tension vs surfactant concentration curve. If \( C_0 \ll 1 \), the equilibrium tension lies on the linear decreasing section of curve and is quite close to \( \gamma_{\text{max}} \). On the other hand if \( C_0 \gg 1 \) the equilibrium tension lies on the flat barely changing section of curve, and is quite close to \( \gamma_{\text{min}} \).

Having now specified a suitable surface tension model, it is desired to find criteria when this model might or might not admit T1 topological transformations.

If topological transformation is to be avoided indefinitely, then it is expected that the vertex location \( X_v \) finds a final asymptotic position in the limit as applied shear \( s \) becomes large.

If the final asymptotic position is only just barely a distance \( e/2 \) from film midpoint \( M_B \), this then is a necessary condition for just barely avoiding a T1.

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**FIG. 15.** Nonlinear surface tension model given by Eq. (37) for various \( \hat{\gamma} \) values. The vertical lines indicate where on the nonlinear curve the physicochemical equilibrium state \( c = 1 \) lies for either \( C_0 = 1/2 \) (leftmost), \( C_0 = 1 \) (middle), or \( C_0 = 2 \) (rightmost vertical line).
In this state (see Fig. 16) film A pulls rightward with tension $\gamma_{\text{max}}$, film B pulls leftward with tension $\gamma_{\text{min}} \equiv \tilde{\gamma}\gamma_{\text{max}}$, while film C also pulls leftward with an intermediate tension,

$$\gamma_{\text{max}}(\sqrt{3} + C_0\tilde{\gamma})/(\sqrt{3} + C_0).$$

Balancing the leftward and rightward pulls requires

$$\tilde{\gamma} = \frac{C_0}{\sqrt{3} + 2C_0}.$$  \hspace{1cm} (39)

The following conclusions (which are also summarized in a phase diagram Fig. 17) can be reached.

If $C_0 \gg 1$, topological transformations cannot be avoided if $\tilde{\gamma} > 1/2$. The net leftward pull due to films B and C is now at least $2\gamma_{\text{min}}$, and when $\tilde{\gamma} > 1/2$ this always exceeds the net rightward pull $\gamma_{\text{max}}$ on film A.

As $C_0$ decreases, it becomes increasingly difficult to avoid topological transformation. The tension in film C now migrates away from $\gamma_{\text{min}}$ towards $\gamma_{\text{max}}$. It is now possible for the net leftward pull of films B and C to exceed the rightward pull of film A even with

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FIG. 16. Tensions in films A, B and C in the case where a T1 event is just barely avoided. Film midpoints $M_A$, $M_B$, and $M_C$ and the vertex location $X_v$ are also shown. The vertical scale has been exaggerated for clarity: Strictly speaking all films should be nearly horizontal in this limiting case.

FIG. 17. Phase diagram indicating when T1 events occur or do not occur according to the nonlinear surface tension model equation (37). The leftward and rightward pulls on the vertex in each region of the phase diagram are indicated schematically: The maximum (rightward) pull on film A is $\gamma_{\text{max}}$; the minimum (leftward) pull on film B is $\gamma_{\text{min}}$ with $\tilde{\gamma} = \gamma_{\text{min}}/\gamma_{\text{max}}$; and the (leftward) pull on film C is close to $\gamma_{\text{max}}$ (if $C_0 \ll 1$) but close to $\gamma_{\text{min}}$ (if $C_0 \gg 1$). Leftward pull exceeding rightward pull implies a T1.
comparatively modest tensions in film $B$, i.e., even with comparatively small $\dot{\gamma}$. Indeed, for $C_0 \ll 1$, topological transformation cannot be avoided if $\dot{\gamma} > C_0/\sqrt{3}$.

The above constitute sufficient conditions for inducing T1s, but might not be necessary conditions—since we have only analyzed the asymptotic limit of large imposed strain—and not the possibility of a T1 occurring for finite strain. Nevertheless the general picture is clear. By considering a nonlinear film tension model Eq. (37) which saturates at some finite tension value in the limit of large surfactant concentration, it is far easier to induce a T1 than for a linear film tension model such as Eq. (2).

V. CONCLUSIONS

The rheology of a 2D hexagonal foam has been considered following the ideas of Princen (1983). Under the action of imposed shear, the nature of the resulting topological transformations or T1 events has been studied.

As a generalization of Princen’s model, the sheared hexagonal foam has been treated as a nonequilibrium system, in the presence of a (physicochemical) dissipation mechanism involving surfactant exchange. Specifically exchange is assumed to take place only between a nonequilibrium film surface and an equilibrium surfactant reservoir. Exchange between a film surface and the surfaces of its neighbors is neglected (this neglect is likely to exaggerate surface tension differences between films).

Within the modeling framework considered here, a Deborah number has been identified as the dimensionless parameter measuring the extent of departure from equilibrium. Foam models exhibiting such departures from physicochemical equilibrium have been little studied compared to models departing from static mechanical equilibrium in the presence of viscous dissipation. The generic features of those widely studied viscous models of foam, and how the model predictions depend on the Capillary number (the mechanical equivalent of the Deborah number) have already been summarized at the start of the paper.

Those generic features, however, carry over in an entirely analogous fashion to the physicochemical dissipation models. Specifically, we have found (paraphrasing the introduction):

- The onset of the topological transformation is delayed by surfactant accumulation. The amount of this delay is determined by a governing dimensionless parameter, the Deborah number, which measures the product of an applied shear rate and a characteristic surfactant equilibration time.
- The time interval between T1 transformations is set by the reciprocal of the shear rate. Meanwhile the duration of an individual T1 transformation is set by the surfactant equilibration time. When the Deborah number is small, one sees therefore a Princen model punctuated by intermittent non-Princen T1 relaxations.
- When the Deborah number is large, energy is injected into the sheared foam faster than surfactant equilibration permits it to relax. Considerable film elongation can occur, which may lead to film bursting.

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NOMENCLATURE

\[ A_{\text{cell}} \] area of a unit cell (made dimensionless with respect to the square of the film length in a regular hexagonal honeycomb)

\[ C_0 \] parameter in a nonlinear film tension model (the ratio between the equilibrium surface concentration of surfactant, and the typical surface concentration at which the variation in film tension reduces significantly)

\[ c, c_B \] the surface concentration of surfactant on a film (made dimensionless with respect to the equilibrium surface concentration)

\[ D e \] the Deborah number

\[ e_x, e_y \] Cartesian unit vectors

\[ L, L_A, L_B, L_C, L_C^0 \] a film length (made dimensionless with respect to the film length in a regular hexagonal honeycomb)

\[ M_A, M_B, M_C \] prescribed positions of film midpoints (made dimensionless with respect to the film length in a regular hexagonal honeycomb)

\[ N, N_A, N_B, N_C \] the surface coverage, i.e. amount of surfactant contained on a film surface (made dimensionless with respect to the amount of surfactant at equilibrium concentration covering a film with length equal to that in a regular hexagonal honeycomb)

\[ s \] the imposed strain

\[ s_f \] a final strain in excess of the Princen yield strain

\[ s_p \] the Princen yield strain

\[ s_{T1} \] the strain to topological transformation (which may differ from the Princen yield strain owing to finite liquid fraction and/or nonequilibrium effects)

\[ t_A, t_B, t_C \] unit tangent vectors

\[ t \] the elapsed time (made dimensionless with respect to the characteristic time scale for surfactant equilibration)

\[ t_p \] the elapsed time at which the Princen yield strain is attained (made dimensionless with respect to the characteristic time scale for surfactant equilibration)

\[ X_v \] vertex position (made dimensionless with respect to the film length in a regular hexagonal honeycomb)

\[ \varepsilon \] the liquid fraction quantified as the cut-off film length at which a topological transformation occurs (made dimensionless with respect to the film length in a regular hexagonal honeycomb)

\[ \delta s \] a small strain increment below the Princen yield strain

\[ \Gamma \] the change in film tension with respect to change in surface concentration of surfactant (made dimensionless with respect to the ratio between equilibrium film tension and equilibrium surface concentration)

\[ \gamma, \gamma_A, \gamma_B, \gamma_C \] film tensions (made dimensionless with respect to the equilibrium film tension)

\[ \gamma_{AC} \] the resultant tension of two films A and C (made dimensionless with respect to the equilibrium film tension)

\[ \gamma_{\text{max}}, \gamma_{\text{min}} \] maximum and minimum film tensions in a nonlinear film tension model, corresponding, respectively, to low and high surfactant concentrations (made dimensionless with respect to the equilibrium film tension)

\[ \dot{\gamma} \] the ratio \( \gamma_{\text{min}}/\gamma_{\text{max}} \)

\[ \sigma_{xy} \] shear stress (made dimensionless with respect to the equilibrium film tension, and the film length in a regular hexagonal honeycomb)
References


