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Characterisation, Modification & Mathematical Modelling of Sudsing

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Abstract

A programme of research is outlined which considers the foaming performance and foam behaviour of surfactant systems commonly encountered in hand-wash laundry detergent applications. An experimental study of the physical chemistry of foam generation indicates that precipitation of a typical anionic surfactant with calcium forms mesophase particles and causes a marked reduction in the rate of transport of surfactant to air-water surfaces and a concomitant reduction in foaming. Oily soil antifoam effects are however insensitive to the presence of calcium, being equally effective regardless of pH and calcium content. They may be reproduced by a simple particle-oil mixture of a saturated and an unsaturated triglyceride (e.g. tristearin and triolein respectively). A detailed foam rheometry study is performed using foam flowing through a constriction. Bubble shapes are used to deduce the normal and shear stresses across the foam flow field. Broad agreement between the experimental stress field and that obtained from quasi-static simulations is demonstrated. As foam flow-rate increases, a different model, which takes explicit account of viscous dissipative forces within the foam flow field is required. The dissipative foam flow model predicts differential shrinkage and stretch rates of foam films. Coupled to a model for surfactant transport, this shows the extent to which surfactant concentration accumulates in shrinking films and is depleted in stretching films. In addition to film stretching, it is also important to know about film bursting or failure rates. Here failure rates are estimated using capillary suction pressures exerted on the films by Plateau border channels around film edges. The failure rates can then be employed to predict the evolution of bubble size at various spatial locations in a foam: reasonable agreement with experimental bubble size distributions is obtained.

Key words: Foams, surfactant chemistry, fatty soils, foamability, rheometry, dissipative effects, continuum modelling

1 Introduction

Household and personal care products derive their effect from the presence of surface active agents or surfactants. These surfactant molecules lower the surface energy/interfacial tension between a hydrophobic phase (e.g. fatty soils, dirt or grease) and an aqueous phase (employed for cleaning), thereby enabling the efficient removal of the former. The decreased interfacial tension reduces the energy penalty for creating additional interphase surface under mechanical agitation in the presence of air. As this happens, the surfactants also dramatically increase the stability of any newly created surface, by providing disjoining and/or surface rheological forces, which resist the breakdown of thin liquid films: foaming or sudsing is the inevitable result [1, 2].

Foams are not only important in their own right, but also as an exemplar of a multi-phase dispersion, other examples being emulsions, creams and pastes. Such dispersions are ubiquitous in household and personal care consumer products. Indeed consumers often judge the effectiveness of a household or personal care product according to the multi-phase dispersion it produces: the volume (e.g. foamability/stability), appearance (e.g. bubble size/liquid content) and tactile properties (e.g. rheology/drainage) are all deemed important [3, 4]. For example in the case of foam produced when washing textiles by hand say, consumers tend to be particularly demanding of the sudsing performance of the products they employ. They require that suds are formed rapidly up to a reasonable volume upon agitation of the detergent product with the aqueous phase. They expect to see a creamy lather consisting of fine bubbles, rather than a more tenuous froth with a larger bubble size. Moreover as consumers interact directly with the froth, tactile properties are of central importance.

In order to design and formulate foam products (and by extension more general multi-phase products) that perform according to consumer expectations, a fundamental understanding of the sudsing process is required. Such understanding must be obtained at many levels, from the underlying physics and chemistry of systems to practical everyday product use. There are also important business drivers behind the product design process. Surfactants constitute a substantial fraction of the cost of current formulations: novel formulations which exhibit the same sudsing behaviour using less surfactant are widely desired by industry.

Foam science addresses these issues by giving insights into how system chemistry controls sudsing behaviour, by providing experimental tools to characterise foams, and by developing mathematical models of foam at a wide variety of length scales and levels of detail. Specifically foam science concerns itself with:

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- Physical chemistry of surfactants and third phase heterogeneities on thin liquid films, which ultimately govern bubble coalescence/bursting and thereby foam stability.
- Physical characterisation of bulk foams, including foam generation, foamability, foam stability and foam rheometry.
- Bubble scale modelling of foam structure and the associated microrheology.
- Continuum level modelling of foam flow and macroscale properties (such as drainage and bursting behaviour).

Important scientific questions still remain in each of these research areas, and particularly in the links between them. It is still not known, for instance, how effectively surfactant can be transported to freshly created air-water film surfaces during foam generation: this is a film surface rheology question. The stability and/or bursting behaviour of these film surfaces can also be affected by water hardness and/or fatty soils. Meanwhile bulk foam rheology is clearly affected by film bursting (bulk yield stress scales inversely as typical bubble size [5]). However bulk rheology is also tied to film surface rheology. Small variations in film interfacial tension (due for example to variations in film surfactant coverage) can suppress bubble rearrangements in flowing foam [6]: the impact on film deformation/stretching and hence on bulk stress, is large. Bubble scale modelling of foam has also predicted large film deformations for rapid imposed shear [7]. This may in turn leave sections of film denuded of surfactant, promoting shear-induced film bursting [6], which catastrophically affects foam volumes: the need to link this back to stability studies on individual films is clear. Continuum models of foams [8, 9] also suffer from a lack of input from phenomena on smaller scales. Although bubble bursting and thereby spatiotemporal variations in average bubble size have been computed via continuum models, empirical criteria for bursting have been employed: critical bubble residence times, critical imposed strains, critical tensions along films, and the like [10]. Only through reference to stability behaviour of individual liquid films can these empiricisms be removed, and a deep mechanistic understanding of sudsing achieved through to an everyday product performance level.

2 A broad approach to foam science

In view of the above shortcomings of current theory, we review below a programme of research that aims to tackle the four areas identified above. This vision is of necessity multidisciplinary in nature, requiring chemists, chemical engineers and physicists among others. We indicate the progress achieved so far, and the likely directions of future advances, moving upwards from the very smallest length scales to a macroscopic end-user level. While we try to adhere to the four research areas specified, it should be recognised that each area informs and is informed by the others. Thus the links between deep mechanistic understanding of foam and practical product design are essential.

2.1 *Physical Chemistry of Sudsing*

In order to study foam physical chemistry, it is first necessary to generate foam! The process of foam generation is characterised by three key interrelated factors – generation methodology, surfactant solution properties, and the antifoam action of deterged (fatty) soil.

2.1.1 *Generation Methodology*

The methodology of consumers in this context simply involves rapid air entrainment into a surfactant solution containing emulsified antifoam materials derived from (fatty) soil. The resulting foam is necessarily polydisperse. Obviously the volume of entrained air, and therefore foam, formed at this stage represents the key point of satisfaction or otherwise of consumers. The stability over prolonged times of the resulting foam is of less immediate significance. Foam tests intended to simulate this aeration process use shaking, tumbling or impinging jets rather than pneumatic methods. We have shown that the initial foam heights measured by two such tests – shaking and tumbling – correlate with a coefficient of ≥ 0.95 for many systems both with and without antifoam. These two methodologies differ significantly in dimensionality, including foam heights for a given system, but are both characterised by high Reynolds numbers ($> 10^5$). The stability of the relevant foam films during air-entrainment using these methodologies cannot therefore be related to the hydrostatic head. If however foam film stability is determined in part by the Plateau border capillary pressure, then the latter cannot therefore be equal to the hydrostatic head (contrast with the case of non-draining equilibrium foams for which hydrostatic head and Plateau border capillary pressure are equal [1, 11, 12]; see also §2.4 below). Further evidence of this is revealed if we consider the effect of the concentration of different soil-based antifoams on foam heights for a given entrainment methodology and surfactant system. Despite differences in antifoam effectiveness of an order of magnitude, the relative amounts of antifoam required to produce given initial foam heights have been found to be independent of that foam height (i.e. plots of foam height against $\log(\text{antifoam concentration})$ are isomorphous). This should not happen if the mechanism for the effectiveness of each antifoam invokes Plateau border capillary pressures *and* those capillary pressures are in turn determined by foam height [13]. We conclude then that either foam film stability during the process of air entrainment, both with and without antifoam, is determined by some other factor than capillary pressure or, more likely, that in the case of such methodology, capillary pressure gradients over foam height are of limited magnitude.

2.1.2 *Surfactant Solution Properties*

Efficient entrainment of air in the absence of antifoam is easily ensured if a sufficient concentration of a suitable micellar anionic surfactant is used and both antifoam and polyvalent ions (e.g. calcium) are absent. Here we have used the usual optimum chain length sodium dodecyl benzene sulphonate ($\text{NaC}_{12}\text{LAS}$) [14] as either a pure surfactant or as an equivalent

commercial blend of chain lengths and isomers. With anionic surfactants the main constraint on effectiveness, in the absence of antifoam, derives from the presence of calcium and other polyvalent ions in hard water which result in the formation of insoluble precipitates. In practice this problem is usually avoided by the addition of a suitable complexing agent (a “builder”). Here we seek understanding of surfactant foam behaviour in the absence of such agents, an interest which reflects the potential cost and environmental disadvantages which can be involved in their use. We have measured the so-called precipitation diagram for $\text{NaC}_{12}\text{LAS}$ where increasing concentrations of calcium in the absence of micelles reveals an apparent solubility product suggestive of 1:2 stoichiometry – the relevant precipitate $\text{Ca}(\text{C}_{12}\text{LAS})_2$ moreover appears to be a mesophase (probably lamellar phase) [15, 16]. Addition of increasing concentrations of calcium to micellar $\text{NaC}_{12}\text{LAS}$ solutions crosses the so-called micellar-precipitation boundary into a phase region where $\text{Ca}(\text{C}_{12}\text{LAS})_2$ precipitate coexists with micelles and monomeric surfactant. This region is essentially invariant according to the (Gibbs) phase rule [17, 18] so that the equilibrium air-water surface tension remains constant with increasing concentrations of calcium and therefore of precipitate of $\text{Ca}(\text{C}_{12}\text{LAS})_2$. By contrast, the dynamic surface tension increases dramatically in this region, reflecting the poor transport properties of the $\text{Ca}(\text{C}_{12}\text{LAS})_2$ precipitate (see Fig. 1). In consequence, foam generation rapidly declines at the micellar-precipitation boundary – reflecting low surfactant adsorptions, low film disjoining pressures and high capillary pressures all conspiring to diminish foam film stability. We should note here that such foam behaviour cannot be reversed by filtration of the precipitate from the solution. The particles of precipitate therefore have no antifoam effect. This is hardly surprising because if they are indeed mesophase entities then we would expect them to be hydrophilic and therefore not to act as antifoam.

2.1.3 Antifoam Action of Deterged Soil

Foam behaviour in this context, and in the absence of precipitation of anionic surfactant by polyvalent metal ions, is often totally dominated by the effect of oily soil. This soil is usually simulated in practical tests with a synthetic mixture of various saturated and unsaturated triglycerides (using for example olive oil and sunflower oil), saturated and unsaturated fatty acids and hydrocarbons. Such a mixture may be realistic but complexity implies a probable lack of clarity in establishing its mode of action. Such clarity is of course not without significance in establishing the limits of possible formulation in eliminating or minimising antifoam action. Here we therefore sought first to find a simpler combination of materials which had essentially the same antifoam behaviour as the oily soil. Then we sought to establish the mode of action of that material. A few studies have made triglyceride/fatty acid combinations as antifoams. The most recent [19] concerned mixtures of triolein and oleic acid. This mixture is a single phase oil. It is without effect unless calcium is present in the aqueous phase and unless the pH is high so that insoluble calcium oleate (‘calcium soap’) particles can be formed at the oil-water interface. The mixture can then function as a typical oil/particle antifoam [20]. Here the function of the particles concerns rupture of the oil-water-air pseudoemulsion film which would otherwise prevent emergence of the oil droplet into the air-water surfaces of foam films. Presence of oil droplets in those surfaces can mean

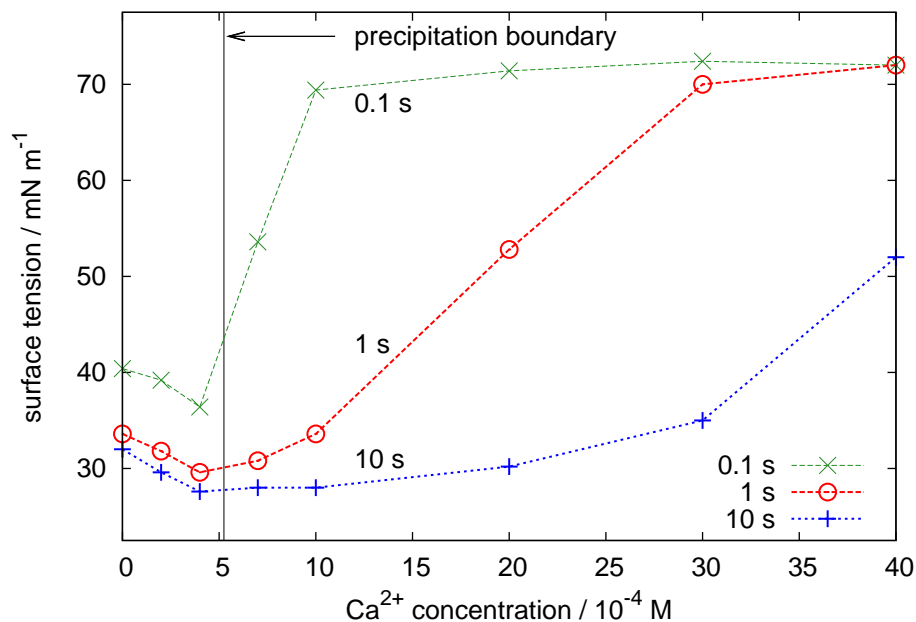


Fig. 1. Dynamic surface tensions vs water hardness at various surface ages of solution of $\text{NaC}_{12}\text{LAS}$: 2×10^{-3} M; NaCl , 1.7×10^{-2} M; $\text{pH} = 10.5$ and Temperature: $25 \pm 1^\circ\text{C}$; \times surface age 0.1 s; \circ 1 s; $+$ 10 s.

formation of unstable bridging configurations leading to foam film collapse [21, 20, 22].

We have found that triolein/oleic acid mixtures do not reproduce the antifoam behaviour of a typical oily soil. Unlike the triolein/oleic acid mixture, the selected oily soil is intrinsically a mixture of oil and particles. It appears to function almost equally well as an antifoam whether or not calcium is present and even at pHs so low that calcium soaps cannot form. This behaviour could however potentially be reproduced with mixtures of triolein/stearic acid and triolein/tristearin. In the case of the former, stearic acid crystals function as the antifoam particle at low pH, sodium stearate particles form at high pH and the absence of calcium, and calcium stearate particles form at high pH and in the presence of calcium. By contrast tristearin is a saturated triglyceride which lacks this chemistry and therefore the complexity, but which is nevertheless a solid of limited solubility in triolein at room temperature.

Both mixtures of stearic acid and tristearin with triolein exhibit the usual behaviour of hydrophobic particle/oil antifoam systems. Thus neither the oil nor the particles alone are effective as antifoams and the presence of particles inverts the emulsion behaviour of the oil from oil-in-water to water-in-oil at high volume fractions of oil. This latter effect is a consequence of rupture of oil-water-oil emulsion films by particles adhering to the oil-water interface. Such behaviour is a necessary corollary of the rupture of the oil-water-air pseudoemulsion films by those particles [20]. We are now investigating the relationship between crystal geometry, contact angle and the stability of those pseudoemulsion films. Measurement of the critical capillary pressure required to rupture such films using the film

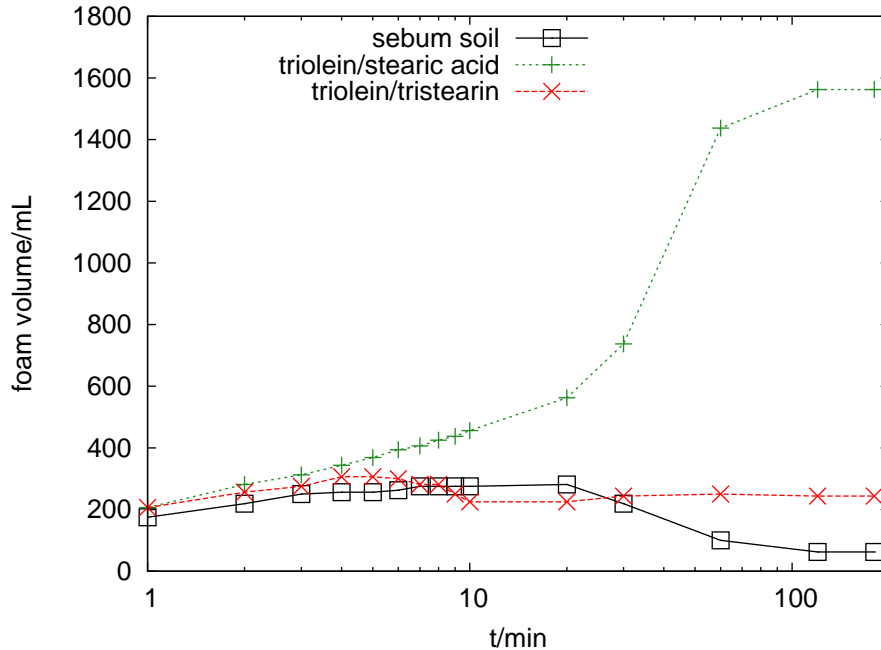


Fig. 2. Evolution of foam volume of sebum soil, triolein/stearic acid and triolein/tristearin antifoams in tumbling tube method under the conditions of $\text{NaC}_{12}\text{LAS}$: 2×10^{-3} M, NaCl : 1.7×10^{-2} M at pH 3, nil Ca^{2+} , Antifoam concentration: 1.0 g l^{-1} and Temperature: $25 \pm 1^\circ\text{C}$; \square In the presence of sebum soil; $+$ In the presence of Triolein/stearic acid; \times In the presence of Triolein/tristearin.

trapping technique of Denkov and co-workers [23, 24] will also form part of that study.

Both stearic acid and tristearin have a small but significant solubility in triolein even at ambient temperature. In preparation of the antifoams it is necessary therefore to avoid the effects of Ostwald ripening on crystal size which would carry the risk of irreproducible antifoam behaviour. We therefore adopted a procedure where the particle-oil mixture was heated to 70°C to form a clear melt. This was then cooled rapidly in an ultrasonic bath at 0°C (before immediate dispersal in surfactant solution). Using this procedure, tristearin formed particles of suboptical size ≤ 0.5 microns. By contrast stearic acid formed large platelets of maximum dimension ~ 50 microns and thickness $\sim 5\text{--}10$ microns. Although exhibiting the same qualitative behaviour as synthetic oily soil the triolein/stearic acid mixtures were significantly less effective. Moreover the antifoam effect with this mixture deactivated rapidly, as shown in Fig. 2, unlike that of oily soil which showed no deterioration in antifoam effect after continuous aeration for more than an hour. By contrast triolein/tristearin mixtures were at least as effective as oily soil and as shown in the figure did not exhibit significant deactivation. Tentatively it seems likely that the differences between triolein/stearic acid and triolein/tristearin at least in part concern the effect of differences in particle size and therefore concentration (i.e. number density). In turn this would be expected to influence probabilities in the processes of antifoam action and deactivation both of which are likely to be, in some measure, stochastic [25].

Characterisation and modelling of the surface, thin film and foam behaviour of these sys-

tems clearly presents challenges. This work therefore relies on the following research to facilitate/identify optimal formulations which achieve the desired foam volume, stability, appearance and tactile properties.

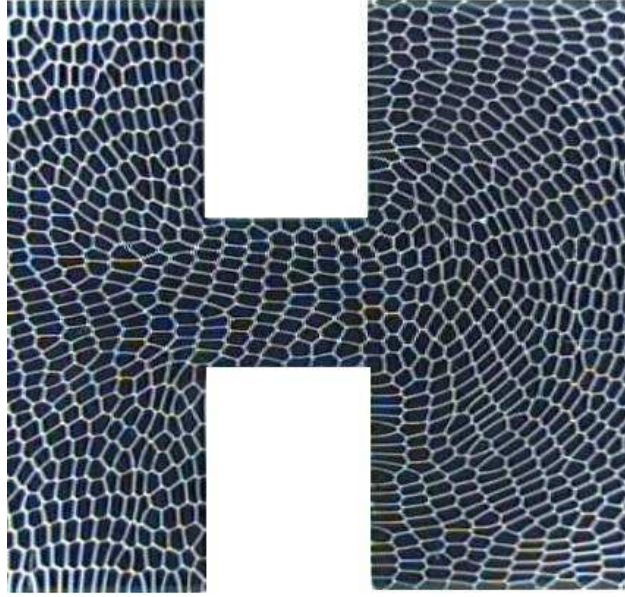
2.2 Foam characterisation through rheometry

The foamability tests referred to above represent only one way in which the foaming performance of a given surfactant could be appraised. Also important is the foam's rheological behaviour which determines tactile properties. With the aim of determining foam performance and robustness in applications, we chose to force foams through a constriction [26], thereby applying extension and shear to the bubbles/soap films. The geometry, size and aspect ratio of a constriction device can be easily varied to probe different regimes of response. For example, small aspect ratio allows examination of two-dimensional flows and individual bubble shape within the foam; large bubble volumes in small devices will allow film-level response to be studied; in another limit, pressure-drop vs flow-rate relationships can be measured for bulk three-dimensional flows. In this way we can ascertain the effects of chemical formulation on stability during flow and the effects of confinement and strain/strain-rate on bubble-size (bubble break-up). In addition, the experiments provide tests of models that purport to describe foam rheology from the film scale upwards.

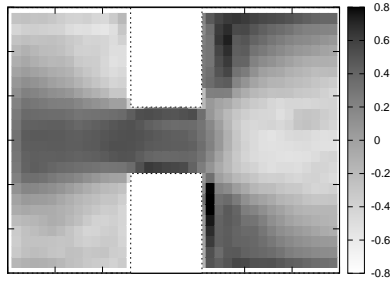
In the experiments reported here, a foam (made in this case using Fairy Liquid instead of $\text{NaC}_{12}\text{LAS}$ as the surfactant) in a channel is forced to flow through a constriction. In these particular experiments, shown in Fig. 3(a), the foam is two-dimensional (2D), i.e. it consists of a monolayer of bubbles confined between two parallel glass plates. The foam channel has width 12 cm and the constriction has a contraction ratio 4:1. The bubble areas are $0.082 \pm 0.021 \text{ cm}^2$, the plate separation is 1.5 mm, the liquid fraction is close to 0.005 and the volumetric flow-rate is 0.05 lpm.

The analysis package ImageJ [27] is used to identify bubble centres and neighbour information (through a so called Delauney triangulation), allowing us to extract the bubble velocities and pressures [28], elastic stress (see Fig. 3(b) and (c)) and strain [29], and the location of the topological changes (i.e. bubble neighbour exchanges) which occur during flow. The regions where the shear and elongational components of the elastic stress, in particular, are high are useful in predicting where soap films may thin most quickly, leading to breakage.

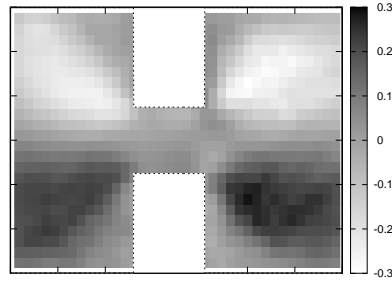
Increasing the flow-rate means that the effect of shear-rate on surfactant motion within and between the films can be felt (surface tension then varies dynamically from film to film, and so films no longer meet one another at 120°), implying that the physical chemistry alluded to above can be made tangible. Additionally, as the plate-separation increases, there is a transition to a three-dimensional foam, and the bulk foams used in applications can be studied, although this introduces greater complexity in the image analysis and therefore interpretation of the results.



(a)



(b)



(c)

Fig. 3. (a) A 2D foam in a channel is forced to flow from left to right through a 4:1 contraction. Soap films are shown as white; via a coarse-graining procedure, these are then used to calculate the components of the stress tensor $\underline{\underline{\sigma}}$ (or more precisely $\underline{\underline{\sigma}}/\gamma$ where γ denotes film tension): (b) extension $\sigma_{xx} - \sigma_{yy}$ and (c) shear σ_{xy} . Experimental values have been normalized by scaling by the square root of the coarse-graining area.

2.3 Bubble-Scale Modelling of Structure of Suds

We model networks of soap films as they move through these benchmark rheological flows. Note that even if the detailed geometric configuration of all the films in a foam sample is observed experimentally, modelling work is still essential in order to understand which microscopic factors determine the resulting rheological behaviour.

In the limit of slow, quasistatic, flows, we have used the Surface Evolver software [30] to simulate a disordered monodisperse foam flowing through the contraction. In the example

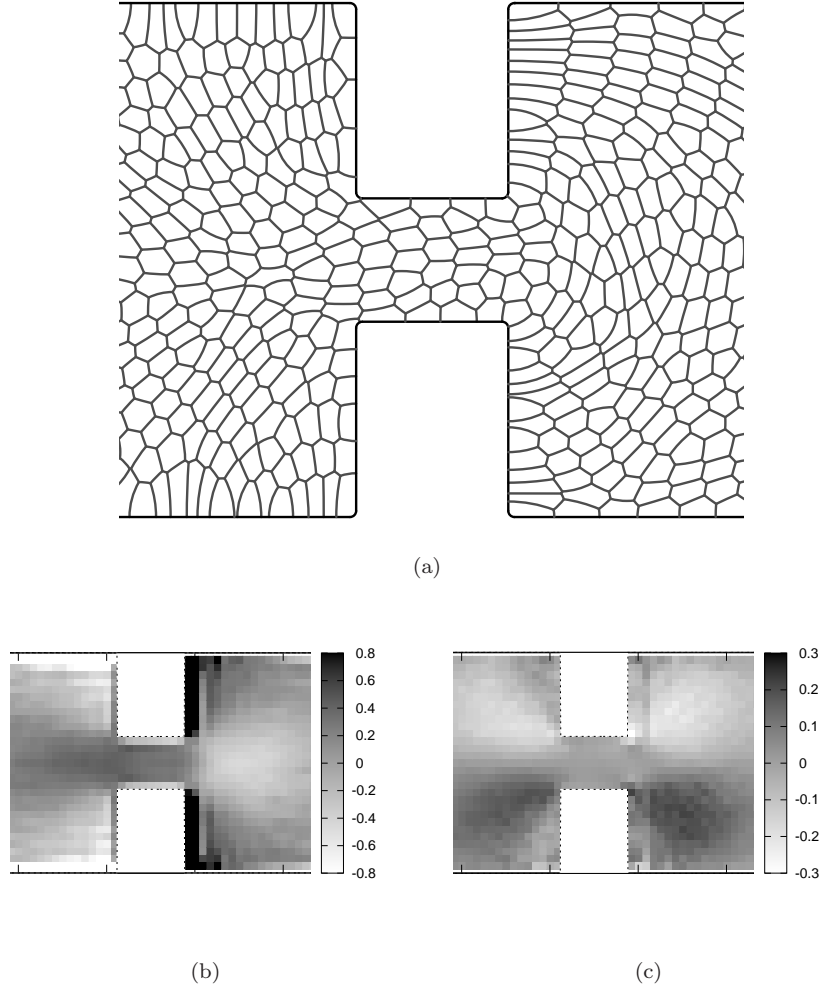


Fig. 4. (a) Quasistatic simulation of a 2D foam flowing through a 4:1 contraction from left to right. The components of the stress tensor for (b) extension and (c) shear can be computed, and compared with the experimental values in Fig. 3.

shown in Fig. 4(a), there are 725 bubbles in a channel with the same dimensions as in the experiment shown in Fig. 3. All quantities of interest can be calculated directly from the simulation, including the bubble pressure and the extension and shear stresses (Fig. 4). Broad agreement is found between the results of Fig. 3 and Fig. 4.

To model flow at the higher shear-rates likely to be encountered in, for example, vigorous agitation in laundry applications, viscous drag terms have significant impact upon the foam rheology and must be included. We chose to do this via the so called viscous froth model [31, 32].

It has been recently demonstrated how the viscous froth model permits the ready computation of shrinkage or stretch rates on individual films [32]. However film shrinkage/stretch rates clearly have an impact on film surfactant concentration: thus a conservation/transport equation for surfactant must be formulated and solved alongside the viscous froth model. The physical ingredients in the surfactant transport equation are (for full details see [33]):

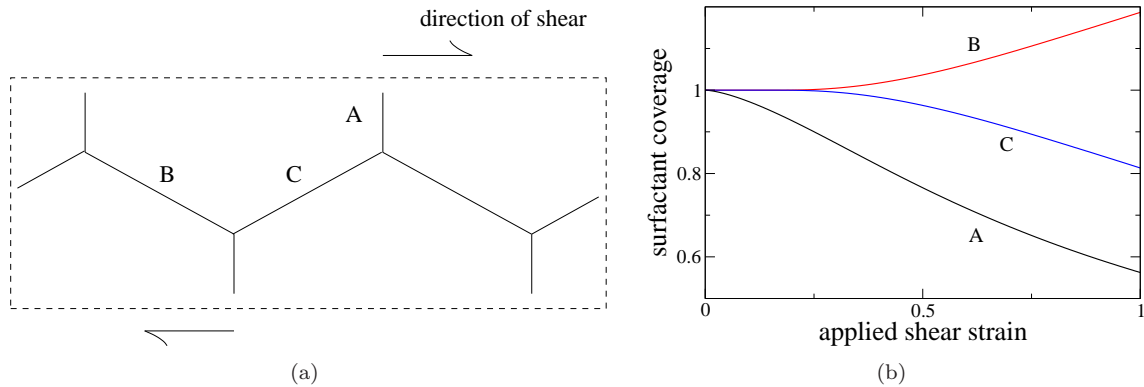


Fig. 5. (a) Sketch of staircase structure and (b) film-averaged surfactant coverage vs applied shear strain. Results are normalised by the surfactant coverage of a quiescent, unsheared film.

- a viscous froth curvature-driven shrinkage of material elements causing surfactant to accumulate,
- an externally imposed shear reorienting and stretching films, and leading to surfactant depletion,
- so called Marangoni stresses produced by gradients in film surfactant concentration which induce tangential film motion that tries to smooth these concentration gradients,
- a relaxation term trying to restore surfactant concentration to an equilibrium value corresponding to liquid-filled Plateau border channels at the edge of a film.

We have initially implemented this viscous froth plus surfactant model on a 2D hexagonal honeycomb or staircase structure, subject to applied shear [7, 34]: see Fig. 5(a).

The behaviour of the resulting system can be characterised in terms of a number of dimensionless groups. These are:

- a capillary number Ca , the product of the applied shear-rate and the characteristic relaxation time for film shape as predicted by the viscous froth model,
- a Marangoni number Mg , the ratio of the characteristic time for film shape relaxation and the time scale for Marangoni forces to smooth gradients in surface tension,
- a Deborah number De , the ratio of the characteristic time for surfactant concentration to relax to equilibrium and the characteristic time for film shape relaxation).

Values of both Mg and De should be informed by the surface rheological measurements (for example by the dynamic surface tension measurements described in §2.1).

Fig. 5(b) shows model predictions of the film-averaged surfactant concentration vs applied shear strain for the three distinct films in the staircase for the case $Ca = 10$, $Mg = 30$ and $De = 100$, values which are typical of laundry wash applications [33]. Film A is directly influenced by the applied shear and its surfactant concentration is depleted as might be expected. The motion of film A induces changes in films B and C (albeit after a short delay). Film B is induced to shrink and its surfactant concentration rises. Film C stretches (and surfactant depletes), but not so dramatically as what is seen for film A. These changes

in surfactant concentration are not the full story however: they induce changes in surface tension which subsequently affect the evolution of film shape via the viscous froth model. Full details will be published elsewhere [33].

2.4 Continuum Modelling and Simulation of Froths and Foams

Ideally the entire foam would be simulated at the scale of the individual bubbles, but the foams found in an actual sudsing system will typically contain substantially more bubbles than can feasibly be simulated in this manner. Here, we therefore concentrate on developing continuum models of foam behaviour.

In particular, the effect of bubble coalescence and bursting on foam stability and the evolution in time of the bubble size distribution within the foam is modelled. We are interested here in stability and evolution over prolonged times after foam generation, not stability during the generation process itself (which has already been addressed in §2.1). Bubble coalescence is modelled statistically using a population balance approach in which the failure rates of films between bubbles of different sizes are calculated in order to predict the evolution of the number density of different sized bubbles.

The population balance model thus requires a model for the stability (or equivalently, failure rate) of an individual film, typically as a function of its size (area), and of the capillary pressure exerted on it by the neighbouring Plateau border channels around its edge [24, 35, 36], though factors such as film stretching rate, local surfactant concentration, etc. could be included. The film failure rate model utilises film drainage times, and accounts for the microscale physical chemistry of films by incorporating a critical maximum disjoining pressure that colloidal thin film forces can produce and sustain [36].

As well as a model for the film stability, a number of topological and geometric properties of the foam are required. These include the average number of faces per bubble as a function of the bubble's volume relative to the average volume at that location in the foam, and also the area of the film between two neighbouring bubbles. Due to their opacity and ephemerality, it is hard to study experimentally the detailed topology of foaming systems. For this reason, three-dimensional simulations with the Surface Evolver [30] were used to investigate the topology of foams with a wide range of polydispersity. From these investigations it was found that the area of a film is most strongly influenced by the volume of the smaller of the two bubbles to which it is attached. This dependency was found to be virtually independent of the underlying polydispersity of the foam [37].

Since the capillary pressure exerted by the Plateau borders on the films is a key aspect of their stability, the population balance modelling needs to be coupled to a foam drainage model describing the Plateau borders [38, 39, 40]. This requires a two-way coupling since the bubble size strongly affects the liquid drainage behaviour. The liquid drainage and growth/collapse rate of the foam are also strongly coupled since the bursting of surface bubbles is caused by the failure of surface films, the rate of which will be directly related to the size of the

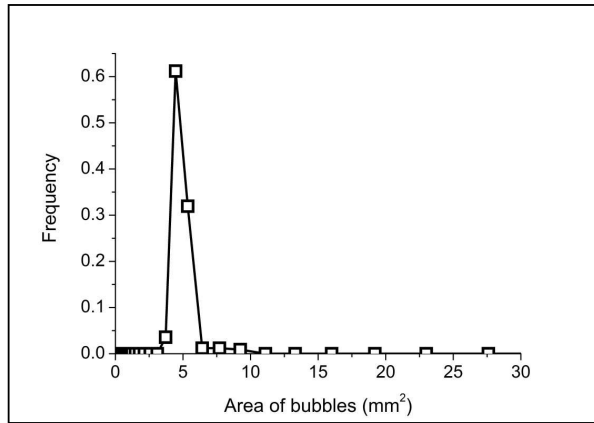
Plateau borders at the bursting surface.

In order to test the modelling approach, the bubble size distributions at a number of different heights in a steady state foam (produced by bubbling air through a SDS surfactant solution with glycerol added to the solvent phase to increase viscosity) were measured experimentally using image analysis. These were then compared to simulated results (see Fig. 6). Since the same film stability model was used for internal coalescence and surface bursting, matching the equilibrium foam height meant that the agreement between the experimental and simulated bubble size distributions was achieved using only a single adjustable parameter (to relate bursting rate and Plateau border capillary pressure, as in [36]).

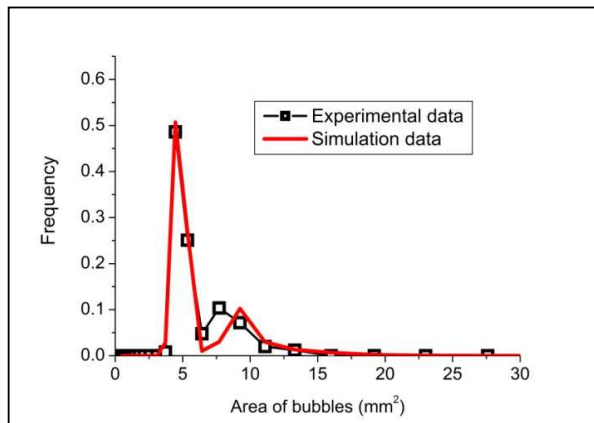
3 Outlook

The programme of research outlined above has helped to advance the area of foam science applied to laundry detergent products. Some key insights of the research programme and open questions are:

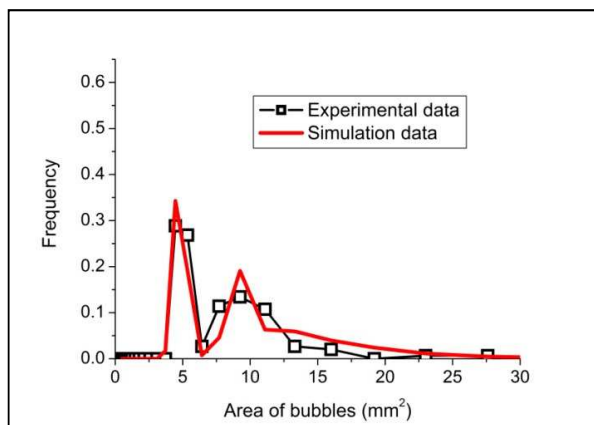
- Our understanding of the processes of air entrainment by shaking, tumbling or jet impingement and the stability of the resultant foam films, both in the presence and absence of antifoam, is limited. It would seem that capillary pressure gradients, perhaps unsurprisingly, are of little significance in the case of the process of foam generation by such methodology. Understanding of effects due to slow transport of surfactant to air-water surfaces during these processes of air entrainment is also inadequate – the intensity of (film level) convection, potential contribution of inertia and the relevant time scales for surfactant adsorption have no adequate experimental or theoretical basis. Thus we have, for example, no basis upon which to compare the time scales of the dynamic surface tensions shown in Fig. 1 with a given method of foam generation. It would seem that this whole subject would represent a clear challenge involving imaging techniques (including fluid motion by, for example, PET) and simulation. Perhaps the greatest challenge of all would be to measure the surface tension of the upper air-water surface of a freshly generated foam. By contrast our knowledge of antifoam action in general and oily soil in particular is steadily developing as a result of contributions made by several groups over the past twenty years [19, 20, 22, 41, 42]. Remaining challenges concern the exact role of particle geometry particularly in the case of crystalline particles. We also have no adequate theory or simulation for the process of deactivation of oil-particle antifoams. However perhaps the greatest remaining challenge concerns molecular level understanding of the role of surfactants (and other components such as polymers) in determining pseudoemulsion film stability in the presence of particles.
- We have performed bubble-scale foam rheometry experiments allowing the direct measurement of film shapes, from which extensional and shear stresses can be determined. Experiments are also in broad agreement with bubble-scale simulation results employing a (quasi-static) Surface Evolver model. It remains unclear however the extent to which these bubble-scale results for foam rheology can be represented by a continuum level de-



(a)



(b)



(c)

Fig. 6. Experimental and simulated bubble volume distribution at positions of (a) 0 mm, (b) 260 mm and (c) 380 mm relative to the bottom of the foam.

scription, e.g. using a visco-elasto-plastic foam model [43]. Even if such visco-elasto-plastic continuum constitutive models [44] are found to perform well, numerical challenges remain to implement the visco-elasto-plastic model via e.g. finite element simulations in a complex flow geometry, for which the tensorial nature of the continuum models [45] must be accounted for explicitly.

- We have successfully introduced surfactant transport terms into the viscous froth model and described the resulting behaviour for shear of a simple hexagonal honeycomb staircase structure. We have not yet applied the model to a large disordered collection of bubbles under shear, although there appears to be no barrier to doing so (apart from the fact that the viscous froth is computationally intensive compared to e.g. quasistatic models). The issue however remains that viscous froth describes 2D foams (i.e. bubble monolayers confined between two glass plates) such as those observed experimentally in Fig. 3(a). Fully 3D foams require more sophisticated models. In 3D, going beyond quasistatic rheology, it is not clear precisely which viscous dissipation mechanisms ought to be included in bubble scale models, although interactions between (thin) bubble films and their surrounding (thicker) Plateau border channels are believed to play a role [46]. Likewise it is not clear how potentially very important surfactant effects on the bubble films [47] in 2D should be incorporated in 3D: it is possible that previous studies of variable surface tension flows in thin geometries can point a way forward [48, 49].
- A relation between capillary pressure exerted on foam films and failure rate of foam films can be used to give reasonable predictions of bubble size distributions in foam. However this ignores the fact that foam film bursting is a complex phenomenon [10, 36] which may need to take into account not only film drainage rates [36, 50] and colloidal forces across films [51, 52], but also film surfactant coverage [53, 54], surface rheological properties [55, 56], film hydrodynamic instabilities [57, 58], and such like. The implications for film failure rates are unclear as these multiple effects can operate in competition with one another, e.g. films with a smaller surface area drain faster [36], while those with a larger surface area are more susceptible to instabilities [10, 36]. Simulation studies with more of the above mentioned effects incorporated, and comparison with experiment for a variety of surfactant systems will be required, in order to isolate which film failure mechanisms dominate for any particular system.

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References

- [1] D. Weaire, S. Hutzler, *The Physics of Foams*, Clarendon Press, Oxford, 1999.
- [2] J. J. Bikerman, *Foams: Theory and Industrial Applications*, Reinhold, New York, 1953.
- [3] R. Brummer, *Rheology Essentials of Cosmetic and Food Emulsions*, Springer, New York, 2005.
- [4] C. Wibowo, K. M. Ng, Product-oriented process synthesis and development: Creams and pastes, *AIChE J.* 73 (2001) 2746–2767.
- [5] H. M. Princen, Rheology of foams and highly concentrated emulsions. I. Elastic properties and yield stress of a cylindrical model system, *J. Colloid and Interface Sci.* 91 (1983) 160–174.
- [6] A. M. Kraynik, Foam flows, *Annu. Rev. Fluid Mech.* 20 (1988) 325–357.
- [7] S. J. Cox, A viscous froth model for dry foams in the Surface Evolver, *Colloids and Surf. A, Physicochem. and Engg Aspects* 263 (2005) 81–89.
- [8] E. Janiaud, D. Weaire, S. Hutzler, Two dimensional foam rheology with viscous drag, *Phys. Rev. Lett.* 97 (2006) 038302.
- [9] I. Cheddadi, P. Saramito, C. Raufaste, P. Marmottant, F. Graner, Numerical modelling of foam Couette flows, *Eur. Phys. J. E* 27 (2008) 123–133.
- [10] P. Grassia, S. J. Neethling, C. Cervantes, H. T. Lee, The growth, drainage and bursting of foams, *Colloids and Surf. A, Physicochem. and Engg Aspects* 274 (2006) 110–124.
- [11] E. S. Basheva, D. Ganchev, N. D. Denkov, K. Kasuga, N. Satoh, K. Tsujii, Role of betaine as foam booster in the presence of silicone oil drops, *Langmuir* 16 (2000) 1000–1013.
- [12] H. M. Princen, Pressure volume surface-area relationships in foams and highly concentrated emulsions: Role of volume fraction, *Langmuir* 4 (1988) 164–169.
- [13] P. R. Garrett, to be published (2011).
- [14] P. R. Garrett, P. R. Moore, Foam and dynamic surface-properties of micellar alkyl benzene sulfonate, *J. Colloid and Interface Sci.* 159 (1993) 214–225.
- [15] G. J. T. Tiddy, Surfactant-water liquid-crystal phases, *Phys. Rep.* 57 (1980) 1–46.
- [16] S. Hassan, W. Rowe, G. J. T. Tiddy, Surfactant liquid crystals, in: K. Holmberg (Ed.), *Handbook of Applied Surface and Colloid Chemistry*, John Wiley & Sons, Chichester, c2001, Ch. 21, pp. 465–480.
- [17] M. Modell, R. C. Reid, *Thermodynamics and its Applications*, 2nd Edition, International Series in the Physical and Chemical Engineering Sciences, Prentice Hall, Englewood Cliffs, NJ, 1983.
- [18] J. M. Smith, H. C. van Ness, *Introduction to Chemical Engineering Thermodynamics*, 4th Edition, Chemical Engineering Series, McGraw-Hill, New York, Singapore, 1987.
- [19] H. Zhang, C. A. Miller, P. R. Garrett, K. H. Raney, Mechanism for defoaming by oils and calcium soap in aqueous systems, *J. Colloid and Interface Sci.* 263 (2003) 633–644.
- [20] P. R. Garrett, The mode of action of antifoams, in: P. R. Garrett (Ed.), *Defoaming, Theory and Industrial Applications*, Marcel Dekker, New York, 1993, pp. 1–117.
- [21] P. R. Garrett, Effect of polytetrafluoroethylene particles on the foamability of aqueous surfactant solutions, *J. Colloid and Interface Sci.* 69 (1979) 107–121.
- [22] N. D. Denkov, P. Cooper, J. Y. Martin, Mechanism of action of mixed solid-liquid antifoams. 1. Dynamics of foam film rupture, *Langmuir* 15 (1999) 8514–8529.

- [23] A. Hadjiiski, R. Dimova, N. D. Denkov, I. B. Ivanov, R. Borwankar, Film trapping technique: Precise method for three-phase contact angle determination of solid and fluid particles of micrometer size, *Langmuir* 12 (1996) 6665–6675.
- [24] A. Hadjiiski, S. Tcholakova, N. D. Denkov, P. Durbut, G. Broze, A. Mehreteab, Effect of oily additives on foamability and foam stability. 2. Entry barriers, *Langmuir* 17 (2001) 7011–7021.
- [25] P. R. Garrett, A simple statistical theory for the effect of changes in antifoam concentration on foamability, *Langmuir* 11 (9) (1995) 3576–3584.
- [26] D. M. Binding, K. Walters, On the use of flow through a contraction in estimating the extensional viscosity of mobile polymer solutions, *J. non-Newtonian Fluid Mech.* 30 (1988) 233–250.
- [27] W. S. Rasband, ImageJ, U.S. National Institutes of Health, Bethesda, Maryland, USA, <http://rsb.info.nih.gov/ij/> (1997–2007).
- [28] B. Foley, Reconstruction of two-dimensional foams, Project report, Trinity College Dublin (2001).
- [29] F. Graner, B. Dollet, C. Raufaste, P. Marmottant, Discrete rearranging disordered patterns. Part I: Robust statistical tools in two or three dimensions, *Eur. Phys. J. E* 25 (2008) 349–369.
- [30] K. Brakke, The Surface Evolver, *Exp. Math.* 1 (1992) 141–165.
- [31] N. Kern, D. Weaire, A. Martin, S. Hutzler, S. J. Cox, Two-dimensional viscous froth model for foam dynamics, *Phys. Rev. E* 70 (2004) 041411.
- [32] T. E. Green, A. Bramley, L. Lue, P. Grassia, Viscous froth lens, *Phys. Rev. E* 74 (2006) 051403.
- [33] B. Embley, P. Grassia, Viscous froth simulations with surfactant mass transfer and Marangoni effects: Deviations from Plateau’s rules, Submitted to *Colloids and Surf. A, Physicochem. and Engg Aspects*.
- [34] T. E. Green, P. Grassia, L. Lue, B. Embley, Viscous froth model for a bubble staircase structure under rapid applied shear: An analysis of fast flowing foam, *Colloids and Surf. A, Physicochem. and Engg Aspects* 348 (2009) 49–58.
- [35] K. Khristov, D. Exerowa, G. Minkov, Critical capillary pressure for destruction of single foam films and foam: Effect of foam film size, *Colloids and Surf. A, Physicochem. and Engg Aspects* 210 (2002) 159–166.
- [36] S. J. Neethling, J. J. Cilliers, Modelling flotation froths, *Int. J. Miner. Proc.* 72 (2003) 267–287.
- [37] M. M. Tong, S. J. Neethling, The size of films in dry foams, *J. Phys., Condensed Matter* 22 (2010) 155109.
- [38] G. Verbist, D. Weaire, A. M. Kraynik, The foam drainage equation, *J. Phys., Condensed Matter* 8 (1996) 3715–3731.
- [39] S. J. Cox, D. Weaire, S. Hutzler, J. Murphy, R. Phelan, G. Verbist, Applications and generalizations of the foam drainage equation, *Proc. Roy. Soc. London Ser. A* 456 (2000) 2441–2464.
- [40] P. Grassia, J. J. Cilliers, S. J. Neethling, E. Ventura-Medina, Quasi-one-dimensional foam drainage, *Eur. Phys. J. E* 6 (2001) 325–348.
- [41] V. Bergeron, P. Cooper, C. Fischer, J. Giermanska-Kahn, D. Langevin, A. Pouchelon, Polydimethylsiloxane (PDMS)-based antifoams, *Colloids and Surf. A, Physicochem. and*

- Engg Aspects 122 (1997) 103–120.
- [42] N. D. Denkov, Mechanisms of foam destruction by oil-based antifoams, *Langmuir* 20 (2004) 9463–9505.
 - [43] P. Marmottant, F. Graner, An elastic, plastic, viscous model for slow shear of a liquid foam, *Eur. Phys. J. E* 23 (2007) 337–347.
 - [44] F. Graner, B. Dollet, C. Raufaste, P. Marmottant, Discrete rearranging disordered patterns. Part II: 2D plasticity, elasticity and flow of a foam, *Eur. Phys. J. E* 25 (2008) 371–384.
 - [45] C. Raufaste, S. J. Cox, P. Marmottant, F. Graner, Discrete rearranging disordered patterns: Prediction of elastic and plastic behavior, and application to two-dimensional foams, *Phys. Rev. E* 81 (2010) 031403.
 - [46] T. Okuzono, K. Kawasaki, T. Nagai, Rheology of random foams, *J. Rheol.* 37 (1993) 571–586.
 - [47] M. Durand, H. Stone, Relaxation time of the topological T1 process in a two-dimensional foam, *Phys. Rev. Lett.* 97 (2006) 226101.
 - [48] P. Grassia, G. M. Homsy, Thermocapillary and buoyant flows with low frequency jitter. I. Jitter confined to the plane, *Phys. Fluids* 10 (1998) 1273–1290.
 - [49] P. Grassia, G. M. Homsy, Thermocapillary and buoyant flows with low frequency jitter. II. Spanwise jitter, *Phys. Fluids* 10 (1998) 1291–1314.
 - [50] A. Bhakta, E. Ruckenstein, Decay of standing foams: Drainage, coalescence and collapse, *Adv. Coll. Interface Sci.* 70 (1997) 1–124.
 - [51] A. Sheludko, Thin liquid films, *Adv. Coll. Interface Sci.* 1 (1967) 391–464.
 - [52] J. Israelachvili, *Intermolecular and Surface Forces*, 2nd Edition, Academic Press Ltd, London, San Diego, 1992.
 - [53] V. Cristini, J. Blawdziewicz, M. Loewenberg, Near-contact motion of surfactant-covered spherical drops, *J. Fluid Mech.* 366 (1998) 259–287.
 - [54] J. Blawdziewicz, V. Cristini, M. Loewenberg, Near-contact motion of surfactant-covered spherical drops: Ionic surfactant, *J. Colloid and Interface Sci.* 211 (1999) 355–366.
 - [55] M. van den Tempel, Surface rheology, *J. non-Newtonian Fluid Mech.* 2 (1977) 205–219.
 - [56] D. Langevin, Dynamics of surfactant layers, *Current Opinion Colloid & Interface Sci.* 3 (1998) 600–607.
 - [57] J. L. Joye, G. J. Hirasaki, C. A. Miller, Asymmetric drainage in foam films, *Langmuir* 10 (1994) 3174–3179.
 - [58] J. L. Joye, G. J. Hirasaki, C. A. Miller, Numerical simulation of instability causing asymmetric drainage in foam films, *J. Colloid and Interface Sci.* 177 (1996) 542–552.