Relaxation Time of the Topological $T1$ Process in a Two-Dimensional Foam

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The elementary topological $T1$ process in a two-dimensional foam corresponds to the flip of one film with respect to the geometrical constraints, and is a process by which the structure of an out-of-equilibrium foam evolves. We study both experimentally and theoretically the $T1$ dynamics in a dry two-dimensional foam. The dynamics is controlled by the surface viscoelastic properties of the films (surface shear plus dilatational viscosity, $\mu_s + \kappa$, and Gibbs elasticity ϵ), and is independent of the shear viscosity of the bulk liquid. Moreover, the dynamics of the $T1$ process provides a tool for measuring the surface rheological properties: we obtained $\epsilon = 32 \pm 8$ mN/m and $\mu_s + \kappa = 1.3 \pm 0.7$ mPa $\cdot$ m $\cdot$ s for sodium dodecyl sulfate, and $\epsilon = 65 \pm 12$ mN/m and $\mu_s + \kappa = 31 \pm 12$ mPa $\cdot$ m $\cdot$ s for bovine serum albumin, in good agreement with literature values.

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Foam rheology impacts material processing and products in many industries and so has been the subject of continuous scientific activity over many years [1,2]. An aqueous foam acts macroscopically as a viscoelastic medium, whose flow depends on bulk and surface rheological properties of the phases, which, in turn, depend on its constitutive ingredients (surfactant, polymers, particles), the liquid fraction, the typical bubble size, and the shear rate. At low liquid fractions (a dry foam) bubbles have polyhedral shapes for which local mechanical and thermodynamical equilibria lead to Plateau's laws for the main geometric characteristics: e.g., three films meet at each junction of a two-dimensional foam with equal angles of 120°. Consequently, the rheology and geometry are linked, since as the foam structure is altered, rearrangements occur until a configuration is obtained where Plateau's laws are satisfied.

Any rearrangement in a two-dimensional foam may be regarded as a combination of two elementary topological processes referred to as $T1$ and $T2$ [1]. The $T1$ process corresponds to the "flip" of one soap film, as depicted in Fig. 1, while the $T2$ process corresponds to the disappearance of cells with three sides. From a mechanical point of view, the $T1$ process corresponds to a transition from one metastable configuration to another, after passing through an unstable configuration where four films meet at one junction (actually, for a small but finite liquid fraction, the instability arises slightly before the fourfold vertex is formed [3]). The spontaneous evolution from one fourfold junction to two threefold junctions, which involves creation of a new film, is driven by minimization of the surface area. Various experimental and theoretical studies on the *frequency* of rearrangement events in foams have been conducted [4–8], but little is known about the typical relaxation time associated with such events [9]. Indeed, the dynamics of the relaxation processes is usually neglected in simulations of foams [10,11] even though the rheological behavior of a foam obviously depends on this relaxation time [5]. More generally, to study the evolution of the foam structure, it is necessary to understand the dynamics of the elementary relaxation process.

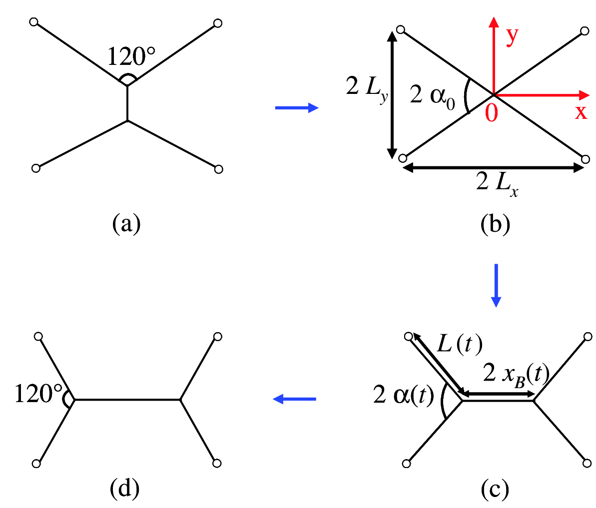

FIG. 1 (color online). Schematic of the $T1$ transition. The initial configuration (a) evolves continuously through metastable states, for which Plateau's laws are satisfied, to an unstable fourfold configuration (b). This unstable state spontaneously evolves into two threefold junctions with creation of a new film (c) until a new metastable configuration (d) is reached, and Plateau's laws are satisfied again. Topologically, the transition between the initial configuration (a) and the final configuration (b) corresponds to a flip of one soap film.

In this Letter we investigate theoretically and experimentally the effect of the viscoelastic parameters on the dynamics of the $T1$ process. Our experiments in a two-dimensional foam show that the relaxation time depends on the interfacial viscoelasticity of the films, but not on the shear viscosity of the bulk liquid. These results are corroborated by a model, which allows for an estimation of the Gibbs elasticity and the surface viscosity of the surfactants used to make the foam.

The experimental setup is depicted in Fig. 2: a dry two-dimensional foam is created in a horizontal Plexiglas cell (1 cm high) by blowing air through a bottle containing a surfactant solution. The polyhedral bubbles created have a typical edge length of 1–2 cm. The liquid fraction in the foam, defined as the total volume of liquid in the Plexiglas cell divided by the cell volume, is about 1%. Two different foaming agents have been used in order to study the influence of the rheological properties of the interface on the $T1$ dynamics: (i) sodium dodecyl sulfate (SDS), at a concentration of 4.80 g/L, forms ''mobile'' surfaces, and (ii) protein bovine serum albumin (BSA), together with a cosurfactant propylene glycol alginate (PGA), both at concentrations of 4.00 g/L, form ''rigid'' interfaces. The impact of the shear viscosity of the bulk liquid has been investigated by adding glycerol, 0%, 60%, and 72% (w/w), to the bulk solutions.

In order to cause rearrangements in the foam, we use a syringe to blow the air away from one bubble. Then the rearrangements are viewed from above with a high-speed camera. The length of the soap film is measured by following its two ends using particle-tracking software. Experiments where the other vertices have noticeable movements during the relaxation process, or where simultaneous $T1$ events occur, have been disregarded.

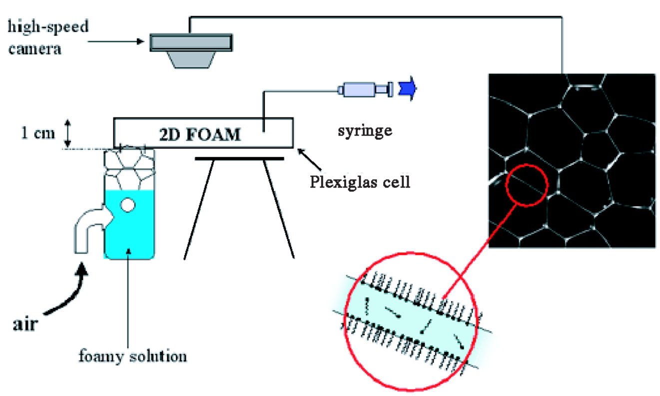

FIG. 2 (color online). Experimental setup: a two-dimensional foam is created in a 1 cm high horizontal Plexiglas cell by blowing air through a surfactant solution. The bubbles are polyhedral with an edge length of 1–2 cm and the liquid fraction in the foam is about 1%. Using a syringe, air is blown away from one bubble, which induces rearrangements, that are viewed from above using a high-speed camera.

The relaxation process is characterized by the creation of a new soap film following the appearance of a fourfold junction. For different surfactant systems, we report the length of the new film, normalized by its final length, as a function of time in Fig. 3. Several trials for each solution are shown and illustrate that the time evolution of the reduced length appears independent of the final film length. We define a typical time T associated with the relaxation process as the time for the film to reach 90% of its final length. A comparison of the results for a foam made with the SDS without glycerol (shear viscosity of the liquid $\mu = 1.0$ mPa · s) and with 60% glycerol ($\mu = 10.7$ mPa · s) shows that there is no significant effect of the viscosity of the bulk liquid ($T \simeq 0.5$ sec for both solutions). This response is not unreasonable since, for the mechanics of a free soap film, viscous effects of the bulk are generally negligible in comparison with the effects of the viscoelastic properties of the interfaces [12,13].

We note that as the foam is constrained between two planes, most of the liquid of each soap film is located in the menisci close to the solid surfaces. In this region there is dissipation that depends on the shear viscosity of the solution. Hence, from our experimental observations we conclude that frictional effects at the boundaries have a negligible influence on the $T1$ dynamics. This result is not in contradiction with the observations made on the rheology of 2D foam [14–16], where a macroscopic stress

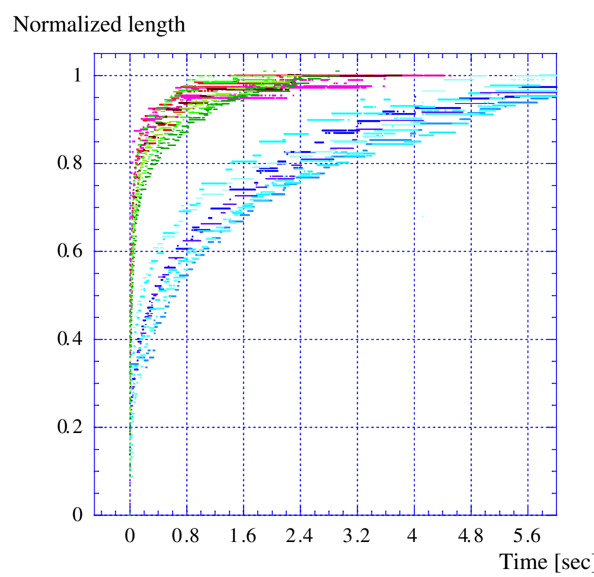

FIG. 3 (color online). Evolution of the film length, normalized by its final length, with time. Each curve represents one experiment. Red curves: SDS solution without glycerol; green curves: SDS solution with 60% (w/w) glycerol; blue curves: BSA/PGA solution without glycerol. The data for SDS solutions with glycerol overlay those without glycerol, which confirms that viscosity of the bulk liquid is not significant. The typical time of the relaxation process, defined as the time to reach 90% of the final length, is about 0.5 sec for the SDS curves and 3.7 sec for the BSA/PGA curves.

(pressure drop) causes motion of the foam relative to the boundaries and the shear viscosity of the bulk solution is the main parameter controlling the dynamics.

Next, we compare the SDS results with those from the BSA/PGA solution $\mu = 7$ mPa · s, both without glycerol. We observe a change in the typical relaxation time by about a factor of 7 ($T \simeq 3.7$ sec for the BSA/PGA solution). Although, coincidentally, the viscosity of the BSA/PGA solution is increased by a factor 7 relative to the SDS solution, we can rule out this influence since we just demonstrated that the viscosity of the solution is not rate limiting. We also verified that the addition of glycerol to the BSA/PGA solution did not produce any significant change in the typical relaxation times (results not shown). These results allow us to conclude that the viscoelastic properties of the interfaces dictate the relaxation time of the $T1$ process.

We now provide a brief description of a theoretical framework for the $T1$ dynamics; for details of the derivation and complete considerations of various special cases see [17]. We compare the theoretical predictions with the experiments, which allows us to extract surface rheological parameters. The net result is a model for the $T1$ process and estimates for the relaxation time.

We assume that the geometry is symmetrical with thin films nearly together at an unstable fourfold configuration; each film connects to one of four fixed vertices at the corner of a rectangle with sides $2L_x$ and $2L_y$ (see Fig. 1). It is experimentally observed that the stretching film has a spatially uniform but time varying thickness $h(t)$ everywhere except near the Plateau borders located at $x = \pm x_B(t)$ at the top and bottom boundaries; these dynamics are common for the fluid dynamics of thin films [18]. We focus on the dynamics of the stretching central film of length $2x_B(t)$, which is driven by the monotonic decrease of the angle $\alpha(t)$:

$$\cos\alpha(t) = \frac{L_x - x_B(t)}{\sqrt{L_y^2 + [L_x - x_B(t)]^2}}. \tag{1}$$

The surface tension γ changes in time as the surfactant surface density Γ is reduced by stretching. Also, we introduce the length $L(t) = \sqrt{L_y^2 + [L_x - x_B(t)]^2}$ of the adjacent films which shorten with time. Since the flat film can support no pressure gradient, the axial velocity $U(x, t)$ in the main body of the film is a linear function of position, $U \propto x$ [18]. This uniform extensional motion means that away from other films we have $\gamma(t)$ and $\Gamma(t)$, which do not change with position x.

The dynamics follow from a force balance on the stretching film and a surfactant mass balance. Neglecting inertia terms and dissipative terms associated with the viscosity of the bulk liquid [17], Newton's second law applied to the film reduces to a balance between surface tension contributions and surface dissipative terms,

$$2\gamma_{\rm eq}\cos\alpha(t) - \gamma(t) - (\mu_s + \kappa)\frac{\partial U}{\partial x} = 0, \tag{2}$$

where μ_s and κ denote the shear and dilatational viscosities and $\gamma_{\rm eq}$ denotes the equilibrium value of the surface tension of the soap solution. During the expansion of the new film, adjacent films act as surfactant reservoirs, so that $\gamma(t)$ and $\Gamma(t)$ are assumed to be close to their equilibrium values, and are related by the Langmuir equation of state: $\gamma(t) = \gamma_{\rm eq} - \epsilon \ln[\Gamma(t)/\Gamma_{\rm eq}]$, where ϵ is the Gibbs elasticity and $\Gamma_{\rm eq}$ is the equilibrium surface density. This equilibrium value $\Gamma_{\rm eq}$ is assumed to be present in the adjacent films, whose surface areas are continuously decreasing throughout the relaxation process.

Next, we turn to a mass balance on the surfactant. This requires accounting for stretching of the interface as well as addition of surfactant to the *new* surface created as the adjacent films, of length $L(t)$, are shortened. We neglect diffusion or adsorption processes from the bulk liquid, restricting our study to short times: For a typical film thickness $h \simeq 40$ μm, the characteristic time scale for diffusive transport from the bulk to the interface h^2/D is roughly 2 sec for SDS, and 16 sec for BSA [19]. Therefore, these slower processes only affect shape adjustments as the final equilibrium is approached. So, the change in the total number of surfactant molecules during a time interval dt is $d(\Gamma x_b) = -\Gamma_{\rm eq} dL$, where $dL = -dx_B \cos\alpha(t)$; here we have only accounted for one interface of each adjacent film as feeding the stretched film since surfactant from the other interface must desorb from the surface, transit through the bulk, then adsorb to the stretched interface, which is a much longer process. Integration of this equation allows us to express $\Gamma(t)$ as a function of $x_B(t)$: $\Gamma(t) = \Gamma_{\rm eq}\frac{L_c - L(t)}{x_B(t)}$, where $L_c = \sqrt{L_y^2 + (L_x - x_0)^2} + x_0$ [$x_0 = x_B(0)$]. In addition, with the above approximations, the density along the film must also satisfy the local conservation law $\frac{d\Gamma}{dt} + \Gamma\frac{\partial U}{\partial x} = 0$. Comparison of these two evolution equations leads to $\frac{\partial U}{\partial x} = \frac{\dot{x}_B}{x_B}[1 - \frac{\Gamma_{\rm eq}}{\Gamma(t)}\cos\alpha(t)]$. Note that since $U \propto x$, the surface velocity at the junction is $U[x_B(t), t] = \frac{dx_B}{dt}[1 - \frac{\Gamma_{\rm eq}}{\Gamma(t)}\cos\alpha(t)]$, which is smaller than the velocity of the junction itself ($= \dot{x}_B$). This velocity difference is a consequence of the slip of the surface (and surfactant) coming from the adjacent film. Finally, Eq. (2) is rewritten as an evolution equation for $x_B(t)$:

$$2\gamma_{\rm eq}\left(\cos\alpha(t) - \frac{1}{2}\right) + \epsilon\ln\left(\frac{L_c - L(t)}{x_B(t)}\right) - (\mu_s + \kappa)\frac{\dot{x}_B}{x_B}\left(1 - \frac{x_B(t)}{L_c - L(t)}\cos\alpha(t)\right) = 0. \tag{3}$$

We now compare this theoretical description with the experiments using measurements of $x_B(t)$. From Eq. (3), a plot of $Y(t) = \frac{\dot{x}_B}{x_B}[1 - \frac{\Gamma_{\rm eq}}{\Gamma(t)}\cos\alpha(t)]/[\cos\alpha(t) - \frac{1}{2}]$ versus

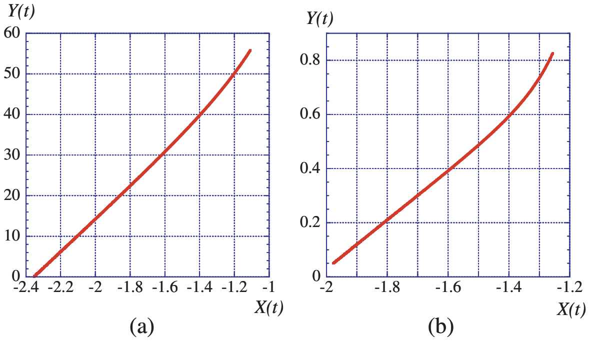

FIG. 4 (color online). Typical plot of the experimental data (Fig. 3) reported as $Y(t) = \frac{\dot{x}_B}{x_B}[1 - \frac{\Gamma_{\rm eq}}{\Gamma(t)} \cos\alpha(t)]/[\cos\alpha(t) - \frac{1}{2}]$ versus $X(t) = \ln(\frac{L_c - L(t)}{x_B(t)})/[\cos\alpha(t) - \frac{1}{2}]$; (a) SDS and (b) BSA/PGA. Note the nearly linear evolution in time, which is in good agreement with the theory. A linear fit of these curves gives estimates of the surface Gibbs elasticity and the sum of the surface and dilatational viscosities.

$X(t) = \ln(\frac{L_c - L(t)}{x_B(t)})/[\cos\alpha(t) - \frac{1}{2}]$ should yield a straight line: $Y = \frac{2\gamma_{\rm eq}}{\mu_s + \kappa} + \frac{\epsilon}{\mu_s + \kappa} X$.

Typical experimental curves $Y(t)$ vs $X(t)$ are shown in Fig. 4 for SDS and BSA/PGA [20]. At short times (less than 0.1 sec for SDS and 0.8 sec for BSA), their evolution is nearly linear, in excellent agreement with the theory. A linear fit of the experimental data plotted in this way allows determination of $\mu_s + \kappa$ and ϵ, using established equilibrium surface tension values of SDS and BSA (38 mN/m [19] and 55 mN/m [21], respectively). We obtained $\epsilon = 32 \pm 8$ mN/m and $\mu_s + \kappa = 1.3 \pm 0.7$ mPa $\cdot$ m $\cdot$ s for SDS, and $\epsilon = 65 \pm 12$ mN/m and $\mu_s + \kappa = 31 \pm 12$ mPa.m.s for BSA/PGA, which are in good agreement with values reported in the literature (e.g., [22,23]). Note, however, that our value of the surface viscosity of SDS correspond to the highest value reported in literature [22], which, in both studies, may be a consequence of the rapid surface stretching giving rise to some nonlinear or inertial effects. In addition, there is a large difference between values of the shear and dilatational surface viscosities, and it is often unclear in published works which surface viscosity is actually measured.

This study of the $T1$ dynamics in a two-dimensional foam illustrates that the relaxation time T associated with the process is a function of two parameters, $\frac{\mu_s + \kappa}{\gamma_{\rm eq}}$ and $\frac{\mu_s + \kappa}{\epsilon}$. From dimensional analysis of Eq. (3), $T = \frac{\mu_s + \kappa}{\gamma_{\rm eq}} f(\frac{\epsilon}{\gamma_{\rm eq}})$, where f is an increasing function of the dimensionless parameter $\frac{\epsilon}{\gamma_{\rm eq}}$. This theoretical description, which has been corroborated with our experimental data, might be useful for simulations of aging or rheological properties of foams. Finally, in agreement with Ref. [5], we expect that a sheared foam has a different rheological response when the shear rate is significantly different than this typical relaxation time.

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