# Flowing Crystals: Nonequilibrium Structure of Foam

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Bubbles pushed through a quasi-two-dimensional channel self-organize into a variety of periodic lattices. The structures of these lattices correspond to local minima of the interfacial energy. The ''flowing crystals'' are long-lived metastable states, a small subset of possible local minima of confined quasi-two-dimensional foams [P. Garstecki and G. M. Whitesides, Phys. Rev. E **73**, 031603 (2006)]. Experimental results suggest that the choice of the structures that we observe is dictated by the dynamic stability of the cyclic processes of their formation. Thus, the dynamic system that we report provides a unique example of nonequilibrium self-organization that results in structures that correspond to local minima of the relevant energy functional.

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There is clear division between the equilibrium and the nonequilibrium processes of self-organization. In the first case, irrespectively of the details of the interactions between the constituents of the system, it assumes a configuration corresponding to the minimum of the relevant free energy functional. For nonequilibrium processes such a unifying ''extremum'' principle is not yet available [1–3]. It is nonetheless clear that the language of energies is, for the dynamical systems, inadequate. Taking just two of the few paradigm examples: although it is possible to rationalize formation of patterns in the convective [4,5] or reactive [6,7] systems, in neither of them it is possible to even identify the spectrum of energies of the resulting patterns. Here we show a model system—a system that produces a set of distinct structures of confined quasi-two-dimensional foams—that couples the dynamics of formation of the structures with their interfacial energies. The foams produced in our system are metastable; their architectures correspond to local minima of interfacial energy. Yet they are not created through a process of relaxation of the interfacial energy from an initially random arrangement. These structures are an immediate result of a process of placing new bubbles into the channel already occupied by ordered foam: a process that can be viewed as a limit cycle of the system. The stability of these limit cycles, corresponding to different lattices, can be altered by a change of the rate of flow of the fluids through the device.

Foams—for the ease of their visualization, and the simplicity of their free energy functional—have been important as a model system in identifying the selection principles that guide formation of patterns. Foams served for experimental verification [8–11] of conjectures on the famous problem of minimization of the interfacial area of tiles filling either a two- [12] or a three-dimensional [8,10,11] space. It has been recently shown [13] that confinement of foams brings out a variety of structures that are not observed without the presence of boundaries. Here we show that foams might also serve as a model system in the study of dynamic pattern formation.

We generate bubbles using a flow-focusing device (FFD) [14] [Fig. 1(a)] that comprises a planar network of ducts of rectangular cross section [15] and uniform height $h = 25\ \mu$m. The heart of the FFD is formed by a junction of three inlet channels: the two outer channels supply the liquid [an aqueous solution of the surfactant Tween 20 (2 wt. %)] at a net rate of flow $Q$ (supplied from a syringe pump Harvard Apparatus PhD 2000), and the central inlet delivers gas (nitrogen) at an externally controlled pressure $p$. The syringe pump delivers significantly fluctuating pressure, and in order to reduce these fluctuations, we also used a pressurized container to deliver the liquid [16]. Liquid and gas form an interface at the junction,

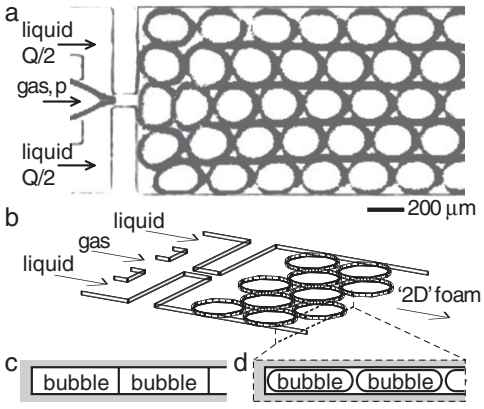


FIG. 1. Experimental system. (a) An optical micrograph of the FFD (the width of the outlet channel is $w = 1$ mm, and the height of the device is $h = 25\ \mu$m). The inlet gas pressure was set to $p = 20$ kPa, and the rate of flow of the liquid (a water-surfactant mixture) to $Q = 0.28\ \mu$L/s. The self-assembled lattice comprises bubbles of nearly circular shapes. (b) A schematic diagram illustrating the aspect ratio of the outlet channel: the bubbles are ''squeezed'' into discoid shapes. For the calculations of the interfacial energy of the lattices, we assume that the interfaces between bubbles are vertical (c). In reality, (d) they are curved because the liquid wets the walls of the microchannel and gas does not contact it.

 

and the stream of gas enters the orifice positioned downstream of the junction, inflates a bubble in the outlet channel, breaks, retracts, and the process then repeats. We monitored the flow with a temporal resolution of 20 $\mu$s using a high-speed camera (Phantom V7).

The bubbles are typically monodisperse, with a coefficient of variation below 2%–3% of the mean diameter [14]; their volume $V$ scales as $V \propto p/Q$, which allows us to maintain a constant $V$ at different rates of flow, provided that we hold the ratio $(p/Q)$ constant [14]. The width $w$ of the outlet channel (here $w = 750$ $\mu$m) is much larger than its height $h$ ($w/h = 30$); typically, the volume of the bubble is larger than the volume of the largest sphere that can be inscribed inside the channel ($V \gg \pi h^3/6$). The bubbles adopt discoid shapes [Figs. 1(b) and 1(d)], and we treat them as essentially two dimensional [Fig. 1(c)]: we refer to the size of the bubble as the effective diameter $d$ of the top interface $d = (4A/\pi)^{1/2}$, where $A$ is the surface area of that interface. Since $A$ does not change upon distortion of the shape of the bubble, only the length $l$ of the its circumference contributes effectively to the interfacial energy $E \approx \gamma(2A + hl)$ of a bubble ($\gamma$ is the interfacial tension).

We approximate the volume fraction $\phi$ of the bubbles by the fraction of the area of the floor of the channel occupied by the bubbles; this approximation neglects the curvature of the interfaces in the cross section of the channel [Figs. 1(c) and 1(d)]. At low values of $\phi$, bubbles flow in disordered packs. At higher values of $\phi$, bubbles assemble into ordered, flowing lattices [14] [the maximum packing fraction of disks on an unbounded plane is $\phi_{\max} = \pi/(2\sqrt{3}) \approx 0.91$; in the presence of the walls, $\phi_{\max}$ is smaller and its value depends on the value of $(d/w)$]. In lattices obtained at $\phi \approx \phi_{\max}$, the bubbles remain circular [Fig. 1(a)]; these structures are determined by elastic shape-restoring interactions between them, and although the system is not in equilibrium, since the shape of the bubbles minimizes their interfacial energy, the geometry of these lattices can be understood—at least locally—in terms of the minimum of their energy. Importantly, for given values of $d/w$ and $\phi$ for which bubbles organize into an ordered lattice, there is a unique structure (either rhombic or hexagonal) that we observe.

For $\phi \approx 1$, the bubbles become significantly distorted, and for any given value of $(d/w)$, we observe a family of distinct, periodic lattices [Figs. 2(a)–2(e)]. The observation of multiple structures for a fixed value of $d/w$ prompted us to pose the following questions: (i) Are the lattices that we observe the only ones that are possible? (ii) What determines which lattice the system produces?

To answer the first question, we enumerated [17] a set of 69 topologically distinct, two-dimensional tessellations of a stripe. This set contained all five [Figs. 2(a)–2(e)] lattices that we observe experimentally, but also other lattices that we did not observe. We optimized the geometry of these lattices for $d/w = 0.2$ (which corresponds to our experiment) to yield the minimum of the total perimeter of the

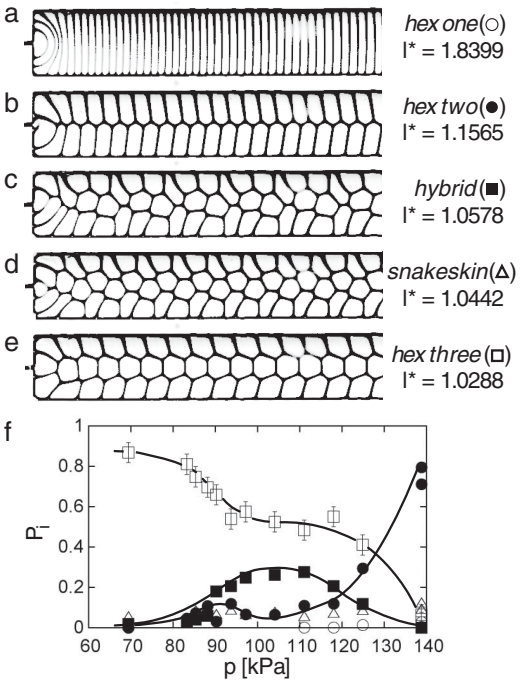


FIG. 2. Flowing crystals. (a)–(e) Optical micrographs of the dynamically self-organized lattices observed at $p = 110$ kPa and $Q = 0.5$ $\mu$L/s ($w = 750$ $\mu$m, $h = 25$ $\mu$m). We call the five observed lattices hex-one (a), hex-two (b), hybrid (c), snakeskin (d), and hex-three (e). We ordered the lattices according to their calculated nondimensional "energy"—a parameter $l^*$ which is the ratio of the total perimeter of the $N$ bubbles comprising the translational unit cell to the total perimeter of $N$ regular hexagons of the same surface area as the surface area of the planar cross section of the bubbles ($l^*$ decreases from top to bottom). (f) The fraction $P_i$ of time that each lattice is produced depends on the pressure $p$ applied to the gas inlet (note that $p/Q = \text{const}$).

bubble-bubble interfaces. The optimization was subject to the approximation of the two-dimensional geometry of the lattice—that is, that the interfaces between bubbles are vertical [17]. Since the curvature of the gas-liquid interfaces in the plane of the cross section of the channel can be assumed to be constant regardless of the shape of the bubble in the plane of the device, the calculations provide a good approximation of the ranking of the interfacial energies of different structures. This approximation, however, fails to describe the stability of lattices in which the length (in the plane of the channel) of at least one of the bubble-bubble interfaces is comparable to, or smaller than, the height of the channel. Within this 2D approximation, for $d/w = 0.2, 31$ structures satisfied [17] the Plateau rules, and we ranked these 31 structures according to their interfacial energies. The experimentally observed lattices are scattered along the list: the *hex-three* lattice had the lowest interfacial energy in the set, the *snakeskin* ranked fourth, *hybrid* ninth, *hex-two* fifteenth, and *hex-one* ranked 31st—it had the highest interfacial energy in the set. The plurality of the lattices that we observe experimentally and their scatter along the energy scale suggest that—as ex-

pected from a nonequilibrium system—the choice of the suite of lattices observed cannot be explained within an equilibrium (energetic) framework.

We explored experimentally whether the selection of the lattices can be altered by changing the total flux of fluids through the device. We formed the lattices of bubbles of constant size ($d \approx 150$ $\mu$m) in an outlet channel of width $w \approx 750$ $\mu$m ($d/w \approx 0.2$) over a range of pressures $p \in$ (70 140 kPa). For each value of $p$, we recorded 5000 images at 10 ms intervals, and counted the number $n_i$ of frames representing each of the five observed lattices. Figure 2(f) illustrates the fraction of frames $P_i = n_i/5000$, corresponding to each structure as a function of the applied pressure. The switching between different lattices probably followed a fluctuation in the pressure applied to the device [16], and was usually followed by a transient period during which the system produced disordered arrays of bubbles. These transients were typically short [16] in comparison to the intervals during which the system produced ordered lattices, and the overall $P_{\text{disordered}} < 0.1$. The ordered structures typically comprised $10^2$ to $10^3$ bubbles, and could be made significantly longer by using a system in which the liquid is fed from a pressurized container [16].

We found that a change of the rate of the flow of the fluids through the device systematically altered the fractions $P_i$ [Fig. 2(f)] [16]. At low pressures ($p = 70$ kPa), we observed primarily the hex-three lattice ($P_{\text{hex-three}} = 0.93$); this lattice has the lowest interfacial energy within the set of observed (and enumerated) lattices. At intermediate pressures ($p \approx 100$ kPa), $P_{\text{hex-three}} \approx 0.6$ and the hybrid lattice was frequently observed ($P_{\text{hybrid}} \approx 0.3$). At the highest pressure probed in our experiment ($p = 140$ kPa), the system produced predominantly the hex-two structure ($P_{\text{hex-two}} \approx 0.8$), but all the other lattices were also observed. Typically, at low rates of flow, we observed structures characterized by lower values of interfacial energies, while at higher rates of flow the system produced lattices corresponding to higher energies more frequently [16]. We note that the statistics of our measurement is rather poor, and that our analysis is qualitative with the sole aim of showing that the probabilities $P_i$ change in a systematic way with a change of the rates of flow of the fluids through the device.

The dependence of $P_i$'s on the rates of flow could arise from the interplay between the rates of relaxation of the geometry of the lattice and of convection of the bubbles through the portion of the channel that we monitored in our experiments. Without any knowledge about the heights of the energy barriers that separate the minima corresponding to the structures that we recorded, we can assess the time scale for a rearrangement along a gradient of interfacial energy. The value of the Ohnesorge number $\text{Oh} = \mu(\rho l \gamma)^{1/2} = 2 \times 10^{-2}$ (for the viscosity of the liquid $\mu = 1$ mPa s, its density $\rho = 10^3$ kg/m$^3$, $\gamma = 30$ mN/m, and a typical length for the rearrangement $l \approx 100$ $\mu$m) indicates that the interfacial dynamics is dominated by inertial effects, and that we can estimate the typical speed of rearrangement of the gas-liquid interfaces as $u_r = (\gamma/\rho l)^{1/2} \approx 1$ m/s. The associated time scale is thus $t_r = l/u_r \approx 100$ $\mu$s, a value that compares well with our experimental observations of rearrangements of the structures in the channel. We also measured the speed $u_c$ at which the lattices flow in the outlet channel [16], to increase linearly with $p$ from $u_c = 37$ mm/s for $p = 63$ kPa to $u_c = 125$ mm/s for $p = 140$ kPa. We calculated the times $t_c$ that it takes for any bubble to be convected from the orifice through our observation window (of length $l_w \approx 5$ mm): $t_c = l_w/u_c$. These times ranged from $t_c = 134$ ms for $p = 63$ kPa to $t_c = 40$ ms for $p = 140$ kPa and were thus always 2 to 3 orders of magnitude larger than the time $t_r$ required for relaxation of the shape of the bubbles provided the system has surmounted the energy barrier. We conclude that barriers dominate the dynamics of relaxation of the structure. This observation is in accord with the common observations that the relaxation of the structure of a foam is a complicated and slow process [18]. We conclude that the fractions $P_i$ faithfully reflect the fractions of time that the system *forms* an observed lattice and are not influenced by the relaxation processes that could change the lattice after it has been formed.

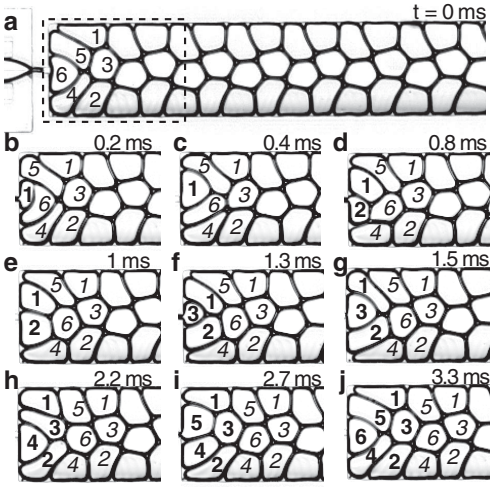


FIG. 3. Optical micrographs illustrating limit cycle of the formation of the lattice. The structure of the lattice acts as a template for the positioning of new bubbles. The process of placing the bubbles is periodic (here period 6 for the snakeskin lattice). The dashed outline in (a) marks the portion of the channel shown in (b)–(j). The time elapsed from the first image (a) is indicated for each inset. The process starts at $t = 0$ (a). We marked six bubbles forming a translational unit cell (the template) with numbers in italic font (a). We also marked the six consecutive bubbles that enter the channel within one limit cycle of the process of formation of the lattice in order of their entry into the channel (from 1 to 6, bold font). After the limit cycle comes to completion, the structure of the foam in the channel (j) is the same as in the beginning of the cycle (a). We acquired the video using the following parameters: $w = 750$ $\mu$m, $h = 25$ $\mu$m, $p = 1.45$ kPa, and $Q = 0.3$ $\mu$L/s.

Since the lattices are periodic, and their geometry is not a result of a process of relaxation from an initially disordered state, they must—and are—formed in periodic processes of placing new bubbles into the channel. This process can be viewed as a limit cycle of the dynamic system that we study. In Fig. 3 we show optical micrographs taken within one period (or cycle) of formation of the snakeskin lattice. The structure in the channel guides the positioning of the bubbles emerging from the orifice: the lattice acts as its own template. There are six bubbles in the translational unit cell, and every sixth bubble is placed in an exactly same manner. The limit cycle is stable: small variations in the size of the bubbles, or in the times at which they emerge from the orifice, do not move the system from its periodic trajectory. Although a similar time sequence could probably be drawn for all the other [17] plausible structures of the quasi-two-dimensional foam, since we do not observe them experimentally, there must be physical mechanisms allowing some cycles and patterns and excluding the others. We postulate that these mechanisms determine the dynamic stability of the different limit cycles corresponding to the ordered structures of foam. We do not provide any analysis of this stability here; we presume that such analysis could be conducted using simulations that successfully reproduce other aspects of motion of foams in microchannels [19].

In contrast to living organisms [20,21], synthetic dynamic systems rarely exhibit the ability to switch among members of a significant set of distinct, accessible, ordered structures. The model system that we presented in this Letter generates an array of structures, and the selection of the type of the ''flowing crystals'' that are generated depends on the speed at which the self-assembly proceeds. We believe that the speed of the flow of the fluids alters the dynamic stability of the limit cycles producing the different lattices. Since we observe very little disordered structure in our experiments, the phase space of the system is likely divided into five basins of attraction—corresponding to the five observed lattices—and the union of these basins covers almost the entire phase space. A sufficiently large perturbation can translate the system from one basin to another, and cause the system to switch to produce a different lattice. This property prompted us to propose the concept of ''dynamic templating'' that describes formation of patterns in which the templates reproduce and the prevalence of one pattern over a different one depends on the relative stability of the corresponding limit cycles.

We have demonstrated a model system that produces a set of metastable, periodic lattices in a nonequilibrium process. The process of formation of these lattices provides a unique example of coupling between the dynamic stability of a limit cycle and an equilibrium property—minimization of energy—of the resulting structures. In this model system it is possible to identify the spectrum of energies of the patterns that are formed in the nonequilibrium processes. The system can be switched between these states with the use of steady-state external control. The self-guided, but externally controllable, growth of periodic structures can, we hope, bring a new perspective to the science of fabrication of regular structures.

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*Note added in proof.*—We would like to point interested readers to a recent work by Raven *et al.* [22] that also studies the flow of dry foams in microchannels.

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