Soap Froth Revisited: Dynamic Scaling in the Two-Dimensional Froth

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In this Letter we study the evolution of a two-dimensional soap froth. We present evidence for the existence of a limiting scale-invariant distribution of the number of sides in a bulk froth at long times. We also discuss the apparent failure of the hypothesis that all internal angles in a froth are 120° and the absence of many-sided bubbles at long times. We also suggest a mechanism to explain the observed exponent describing the rate of area growth.

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In a previous paper, we studied experimentally some aspects of the coarsening of two-dimensional soap froths as model diffusion-driven cellular systems.[1] We identified two regimes: One transient, during which evolution depends on initial conditions, and one asymptotic, during which the average bubble area a grows like a power law $a \propto t^{\alpha}$. While theory and general arguments[1-3] predicted $\alpha=1$, the experimental measurements gave $\alpha=0.59 \pm 0.11$. For bubbles with up to nine sides, the experiments apparently verified the statistical validity of Von Neumann's law,[4] which states that the growth rate of a bubble depends solely on its number of sides, i.e., $da_i/dt=\kappa(n_i-6)$, where κ is a diffusion constant, i indexes a bubble in the pattern, a_i is the bubble's area, and n_i is its number of sides.

In this Letter we characterize in more detail the regimes of evolution of soap froths by studying experimentally the distribution of the number of sides of bulk bubbles (bubbles not touching the outer walls of the cell) $\rho(n)$ and its second moment μ_2 (to be defined below). We present evidence for the existence of a limiting distribution $\rho^*(n)$ with second moment μ_2^* which characterizes the scaling regime of the bulk froth. Aboav had already attempted to characterize froth evolution by means of $\rho(n)$ and μ_2,[5] using data obtained by Smith.[6] He concluded that μ_2 increased indefinitely with time. However, Smith's data did not extend long enough in time to discover the scaling regime, so Aboav based his conclusions on transient states.

We also report systematic variations from the commonly accepted rule that the three membranes at each vertex of the froth meet at 120° angles. While these deviations do not alter the theoretical prediction $\alpha=1$, they may change the rate of evolution for few- and many-sided bubbles, and thus alter the distribution functions like $\rho(n)$ or area distributions. Finally, we discuss the discrepancy between the measured and predicted values of α.

We have described the experimental apparatus and procedure in detail in Ref. 1. We inject a colored soap froth into a thin rectangular plexiglass cell placed level on a photocopier and then we seal the cell. The soap films stretch between the top and bottom plates with fluid accumulating where the films touch the plates (the *Plateau borders*). The Plateau borders are large enough to show up clearly in a direct photocopy. We restrict our analysis to bubbles not in contact with the cell walls and to patterns in which the number of bulk bubbles is at least 3 times the number of bubbles in contact with the walls.

In Fig. 1 we show the second moment of the distribution of number of sides for two experimental runs, starting from different initial conditions. We define the second moment as follows:

$$\mu_2=\sum_n \rho(n)(n-\bar{n})^2,$$

where $\bar{n}$ is the average with respect to the same distribution $\rho(n)$.

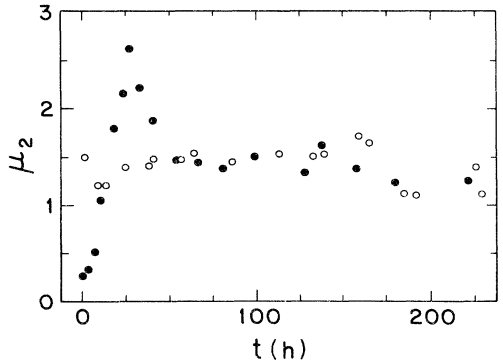

FIG. 1. Second moment μ_2 of the distribution of number of sides $\rho(n)$ vs time in hours for two runs. The first run (solid circles) used helium gas and started from a nearly regular array of hexagons. The horizontal scale has been multiplied by 3 for clarity. The second run (open circles) used air and started from a very disordered pattern. The apparent slight decrease in the last few points is not statistically significant.

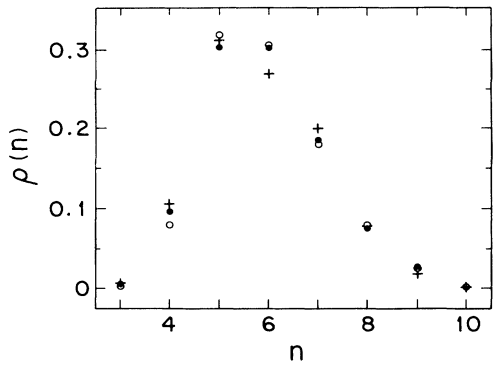

FIG. 2. Distribution of the number of sides $\rho(n)$ of bulk bubbles in the froth for three states in the scaling regime of evolution. The times when these distributions were measured are 15.25 h (open circles), 29.48 h (solid circles), and 32.9 h (crosses). Number of bubbles range from a few hundred to about sixty.

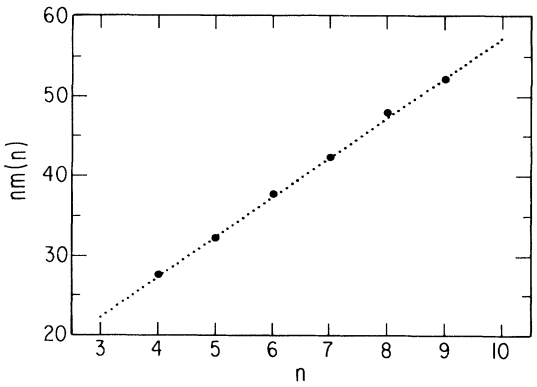

FIG. 3. Average number of sides of the nearest-neighbor interior bubbles adjacent to an n-sided bubble, $m(n)$, times n as a function of n. Solid circles are the experimental data. The straight dotted line is the Aboav-Weaire relation for $a=1$ and $\mu_2=1.4$.

The solid circles correspond to the run labeled (d) in Fig. 1 in Ref. 1. This run used helium gas. It started with approximately 10000 bulk bubbles and ended with 140 bulk bubbles. The initial pattern consisted of large domains of hexagonal bubbles separated by grain boundaries containing both five- and seven-sided bubbles. Since the initial $\rho(n)$ was sharply peaked around six, the corresponding value of μ_2 was very small. As the froth started to evolve, μ_2 increased rapidly, as the bubbles in the grain boundaries grew or shrank according to their number of sides. μ_2 reached a peak when the rate of evolution was maximal, then decreased until all the domains of regular hexagons disappeared. Thereafter (within experimental error) μ_2 had a time-independent value of $\mu_2^*=1.4\pm0.1$ suggesting the existence of an asymptotic scaling regime. The open circles in Fig. 1 comes from a run using air, with disordered initial conditions (approximately 5000 initial bulk bubbles and 100 final bulk bubbles). The initial distribution $\rho(n)$ for this run had a second moment close to the asymptotic one. After an initial transient in which μ_2 decreased slightly, μ_2 eventually reached the same asymptotic value μ_2^* as in the initially ordered run.

Since our system is finite, the average number of sides of all the bubbles in the bulk is not exactly six as required by Euler's law. For patterns with very few bubbles the deviation from six can be large. To further limit edge effects, we measured μ_2 only in patterns with $\bar{n}>5.91$. Our measurements of μ_2 agree with our previously proposed dynamic measure of disorder, $\mathscr{D}$. This parameter is essentially the fraction of the total area of the system occupied by disordered regions. In both runs shown in Fig. 1, μ_2 reached its asymptotic value at the same time that the power-law behavior of area growth set in and $\mathscr{D}$ reached its final value of 1. Note that for initially disordered conditions, $\mathscr{D}$ decreased slightly before increasing to 1 [as shown in Fig. 1(f) of Ref. 1], just as μ_2 did before reaching μ_2^*. μ_2 reaches its equilibrium value while there are still nearly 1000 bubbles, indicating that the equilibration is a true bulk property of the froth. The apparent slight decrease in μ_2 for the last few measurements (total count of approximately 100 bubbles) may be an edge effect (large bubbles which have many sides are more likely to touch the edge and hence be excluded from the average, decreasing the calculated μ_2) but is not statistically significant.

In Fig. 2 we show the distribution $\rho(n)$ as a function of n for three states of an air froth in the scaling regime. Within experimental error the three distributions are the same. We believe this is compelling evidence for the existence of a limiting scale-invariant distribution $\rho^*(n)$ characterizing all states of the froth in the scaling regime. The distribution $\rho^*(n)$ agrees well with that found in several recent computer simulations.[2,7,8]

Another aspect of Aboav's study of froths is the correlation of cell shapes between neighboring bubbles. Mathematically this is expressed by the equation

$$m(n)=6-a+(6a+\mu_2)/n\,,$$

where $m(n)$ is the average number of sides of the neighbors of an n-sided bubble. For $a=1$ this equation is the Aboav-Weaire relation.[9-11] The case $a=1$ and $\mu_2=0$ represents a screening length of one bubble for the *topological charge* $(n-6)$. Aboav checked the validity of this equation in the transient regime and fitted the data with $a=1.2$.[5] In Fig. 3 we show the experimentally measured values of $nm(n)$ (solid circles) for the bulk froth in the scaling regime. The straight dotted line is the Aboav-Weaire result using $\mu_2=1.4$ and $a=1$. The experimental data and the theoretical prediction agree very well.

In the derivation of his law, Von Neumann assumed that all internal angles in the froth are 120° independent of the bubble's number of sides.[4] Since the derivation

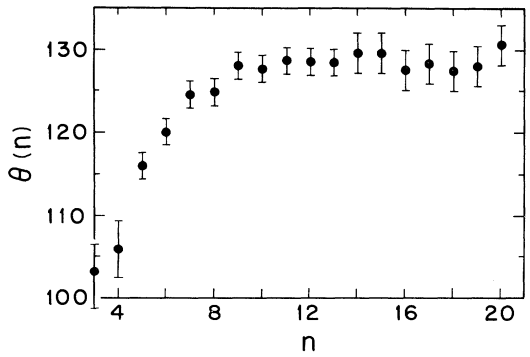

FIG. 4. Average internal angle of bubbles $\theta(n)$ as a function of their number of sides n in an air froth. The error bars denote 1 standard deviation of the measurements. Ten bubbles or more were measured for small n, and fewer for large n.

resulting from this hypothesis is purely local, the variation we observed (in Ref. 1) in rates of bubble growth for different bubbles with the same number of sides was puzzling. We have measured internal angles at vertices as a function of the number of sides by enlarging the individual vertices 10 times, drawing the bisectors of the Plateau borders, and measuring the angles of intersection. We are not able to measure the angle of the soap film directly but we have checked that it is well aligned with the centers of the Plateau borders and that it has no obvious vertical curvature. However, errors of even 10% in centering and vertical flatness would be difficult to observe. We present the measured average internal angles for n-sided bubbles $\theta(n)$ in Fig. 4. We find significant deviations from 120°. The angle deviation appears to be independent of the length scale and the width of the Plateau borders but we have not made exhaustive checks. We conjecture that this deviation is due to nonlinear bending effects in the Plateau borders. Note that the deviation from 120° is such that membranes have a smaller curvature than expected. If we generalize Von Neumann's law to include this effect, we find

$$\frac{da_n}{dt} = -\kappa\left[6-3n\left(\frac{\theta(n)}{90}-1\right)\right],$$

where a_n is the area of an n-sided bubble, and the equation holds only for ensembles of n-sided bubbles. Plugging in the measured values for $\theta(n)$ yields a result close to Von Neumann's law, but with a smaller diffusion constant. Existing experiments cannot distinguish between the two forms of Von Neumann's law.[1,12] We are currently performing a more careful measurement of values for large n.

The variation in angles among bubbles with a given number of sides provides a mechanism for the spread in growth rates among bubbles with the same value of n. One result of the deviation from 120° is the production of a large strain energy in the membrane network, making many-sided bubbles unfavorable. We have tested

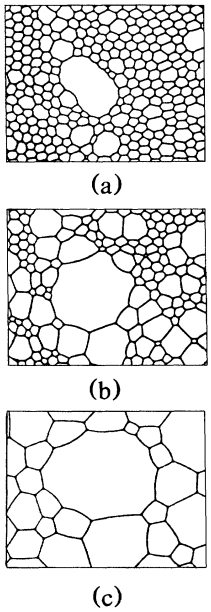

FIG. 5. Typical evolution of a many-sided bubble. Such bubbles gradually lose sides with the evolution of the pattern until they reach 11–12 sides. In this example, the bubble was imposed as an initial condition at the beginning of a run. The detail shown represents about 5% of the total cell area, near the center of the cell.

this by imposing many-sided bubbles in our froths and observing their evolution. In Fig. 5(a) we show a detailed photo of a bubble which initially had twenty sides. Note the large deviation from 120° in the internal angles of the bubble. At the end of the time sequence [Fig. 5(c)] the bubble has twelve sides. While the area equilibrates even when Von Neumann's law and the 120° rule are exactly obeyed, as shown by computer simulations of the microstructural evolution of thin films,[13] the process is much slower. A visible manifestation of the strain in the membrane network due to the violation of the 120° rule is the high frequency of side exchange without bubble disappearance ($T1$ *processes*) occurring near many-sided bubbles.[14] These processes provide an effective mechanism for strain relief. One consequence of this strain is that many-sided bubbles tend to approach each other via a sequence of $T1$ processes. Our data show that pentagonal bubbles in a pattern disappear about 16% of the time by shrinking, 34% by the disappearance of an adjacent bubble, and 50% by $T1$ processes. Of the latter, the majority occur adjacent to many-sided bubbles.

In our previous paper, we observed that the asymptotic state of the soap froth evolved with $\alpha = 0.59 \pm 0.11$ instead of the theoretically predicted $\alpha = 1$.[1-3] We now believe that this deviation from expected behavior may be due to the use of a constant fluid volume, and that our check on the constancy of the Von Neumann–law κ was

not sufficiently sensitive to prove that the change in the exponent was not caused by a decrease in diffusion rates. When a soap froth evolves, the total perimeter of soap films decreases. With a constant fluid volume, the excess fluid accumulates in the Plateau borders, the regions where the soap films adhere to the glass plates. The net effect is to reduce the available area for diffusion in the plane of the films. We do not believe that film thickening is significant since the thickness of the soap films is determined by the competition of an attractive Van der Waals force between the monolayers which compose the film and repulsive electrical double-layer forces, and hence should be approximately constant throughout a run. We have performed preliminary measurements of the broadening of the Plateau borders. The experimental observations show that the area available for diffusion ranges from typically 90% of the spacing between the plates at the beginning of a run to 75% at the end of a run. We have included the Plateau-border thickening in the phenomenological model of Ref. 1 and used it to fit our experimental data. The fits are good and the effect gives a deviation in the right direction and of the right order of magnitude to explain the observed value of α. However, we have not done a full set of measurements to establish the exact relation. We are planning a set of experiments using a drained cell to produce Plateau borders of constant widths.

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