Nonideal effects in the two-dimensional soap froth

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We discuss the effect on two-dimensional bubble growth of deviations in internal vertex angles from the predicted 120°. We also present evidence that Plateau border broadening contributes to the anomalous growth exponent that we have previously observed in froth coarsening.

Most studies of the two-dimensional soap froth have considered it as a model for ideal two-dimensional grain growth. In this role its value has been amply demonstrated.[1-4] We have previously measured the average internal angle at the vertices in a two-dimensional soap froth and found systematic deviations from the predicted value of 120°.[5] We have also characterized the evolution of a two-dimensional soap froth and found that it reaches a *scaling state,* that is, a state in which the distributions of fractional bubble area and number of sides remain constant in time. In the scaling state the average bubble area $\langle a \rangle$ grows as a power law in time, $\langle a \rangle \propto t^{\alpha}$, with growth exponent $\alpha = 0.59 \pm 0.11$.[6] A variety of theoretical arguments predict $\alpha = 1$.[4] In this report we discuss the effect of angle deviations on bubble growth rates and present evidence that film thickening contributes to the deviation of the measured growth exponent from the theoretically predicted value.

We have discussed our experimental procedure in detail elsewhere.[6] The basic apparatus consists of a thin rectangular Plexiglas cell which we fill with a soap froth to produce a two-dimensional pattern, seal, and allow to evolve. To record the pattern evolution, we periodically photocopy the cell and analyze the results by hand.

The driving mechanism behind the pattern evolution of the soap froth is pressure-driven diffusion. If we assume that (1) all vertex angles in a froth are 120°, (2) all walls are sections of circular arcs, (3) the pressure difference across a wall ΔP is proportional to the reciprocal of the radius of curvature of the wall, (4) the rate of gas diffusion across a wall is equal to the product of its length with the pressure difference across it, and (5) pressure differences are small so that diffusion of gas is equivalent to diffusion of area, we obtain von Neumann's law for the rate of change of the area, A_n, of an n-sided bubble[7]

$$\frac{dA_n}{dt} = \kappa(n-6) , \tag{1}$$

where κ is an effective diffusion constant with the units of area/time. von Neumann showed that this law is exact for each bubble in any system obeying these five hypotheses.[7]

If we assume that a pattern's free energy depends only on its wall length and linear functions of wall curvature and that the pattern evolves to minimize the free energy, we find that in an equilibrated pattern the angle at every vertex should be 120°. Since the internal angles of straight-sided polygons with $n \neq 6$ are not 120°, energy minimization requires that bubbles with fewer than six sides have convex walls and bubbles with more than six sides concave walls. Experimentally we have found that at all times the average internal angle lies between 120° and the polygonal angle for straight sides, i.e., bubbles are more polygonal and less curved than predicted by linear energy arguments. Thus there must be an additional nonlinear curvature energy. We can recover a generalized form of von Neumann's law if we assume an n-dependent typical internal angle, $\theta(n)$,[5]

$$\frac{dA_n}{dt} = \kappa \left[3n \left[1 - \frac{\theta(n)}{180^\circ} \right] - 6 \right] . \tag{2}$$

We show the calculated value for the modified von Neumann's law obtained using our previous experimental measurements of $\theta(n)$ in Fig. 1, along with a linear fit corresponding to an unmodified linear relation. In spite of the large angle deviations observed experimentally (up to 10°), dA_n/dt remains a nearly linear function of n, though with a smaller slope than that obtained from the unmodified law with the same value of κ. The scarcity and small size of three-sided bubbles results in a large error for dA_3/dt and the true value is probably larger.

Previous experimental verifications of von Neumann's law have looked only at bubbles with fewer than ten sides.[6,8] In Fig. 2 we show dA_n/dt in an air froth for a pattern with a large range of bubbles sizes and hence number of sides. Since it is not practical to make an experimental cell large enough to generate a 20-sided bubble in a scaling state, we need to use froths with artificially introduced many-sided bubbles. Such nonequilibrium froths may have growth rates which differ from those in a scaling state froth. The indicated error bars are one standard deviation in the measured values of dA_n/dt and at least partially represent real fluctuations in bubble growth rates. For example, some seven-sided bubbles shrink. However, much of the scatter is probably

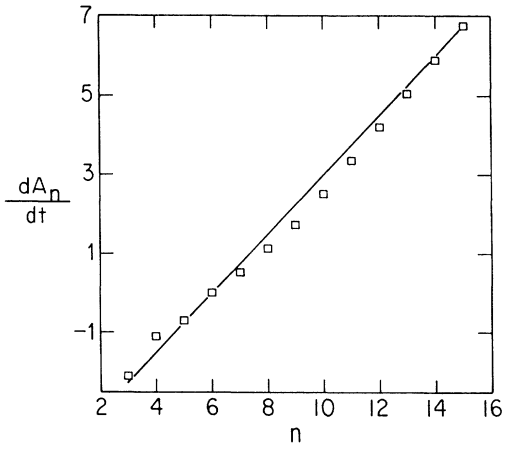

FIG. 1. *Modified von Neumann's law.* Growth rates for n-sided bubbles predicted by the modified form of von Neumann's law [Eq. (2)] using the experimentally measured angle deviations in Ref. 5 (squares) and an unmodified von Neumann's law [Eq. (1)] with the same average diffusion rate (solid line). The large error in the experimental measurement of $\theta(3)$ makes the true value for dA_3/dt uncertain.

due to measurement error rather than intrinsic fluctuations in growth rates. We have discussed sources of measurement error in detail elsewhere.[4] We are interested primarily in the linearity of the measured growth rates as a function of n, so we neglect the absolute value of κ which depends on details such as cell thickness and the total amount of fluid in the froth and hence varies from run to run.

We obtain the expected linear relation between n and dA_n/dt for bubbles with between five and roughly 20 sides. Three- and four-sided bubbles shrink slightly more slowly than expected and bubbles with more than about

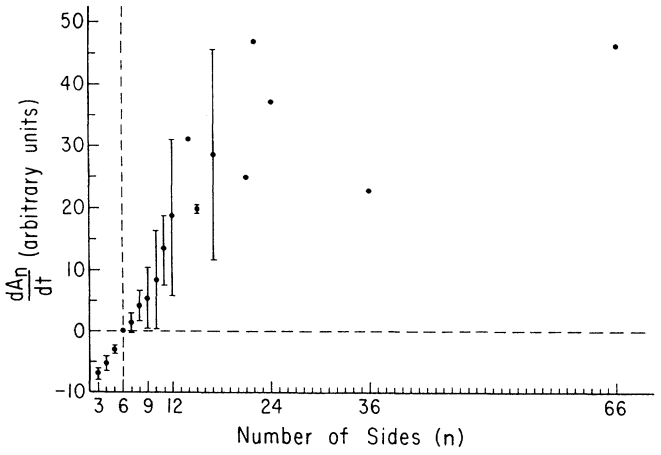

FIG. 2. *von Neumann's law.* Growth rates for n-sided air bubbles. The result shows some features of the modified form of von Neumann's law but is also close to the unmodified form for n up to 24. Error bars show one standard deviation. Single points indicate that only one measurement was made for that number of sides.

20 sides seem to grow slightly more slowly than expected. The apparent slower rate of shrinkage of few-sided and many-sided bubbles and the faster than linear increase with n for bubbles with between 9 and 14 sides slightly favor the modified form of von Neumann's law [Eq. (2)]. However, within experimental error we find agreement with both the modified and unmodified [Eq. (1)] forms of von Neumann's law.

Given the experimental confirmation of von Neumann's law (or its modified form), it is somewhat surprising that we have obtained long-term growth exponents different from 1.[9] von Neumann's law predicts that in a scaling state the average area of a bubble $\langle a \rangle$ should be proportional to the time t.[6,10] Let A be the area of the entire system, N be the total number of bubbles $[\langle a \rangle = A/N]$, $\rho(n)$ as above, and $\lambda_n \equiv \langle A_n \rangle / \langle A \rangle$. Then, assuming the distributions are random, and coarse graining over the time it takes for one bubble to disappear, we find that the average number of bubbles lost per unit time is the area lost by three-, four-, and five-sided bubbles per unit time divided by their mean areas,

$$\frac{dN}{dt} = -\sum_{n=3,4,5} \frac{\kappa \rho(n) N(n-6)}{\lambda_n \langle a \rangle} . \tag{3}$$

Substituting for $\langle a \rangle$ we obtain

$$\frac{dN}{dt} = -N^2 \sum_{n=3,4,5} \frac{\kappa \rho(n)(n-6)}{\lambda_n A} . \tag{4}$$

Since the distribution functions $\rho(n)$ and λ_n are time independent in a scaling state, the sum in Eq. (4) is a constant and

$$\frac{dN}{dt} \propto -N^2 \Longrightarrow N \propto t^{-1} , \tag{5}$$

so

$$\langle a \rangle \propto t . \tag{6}$$

The modified version of von Neumann's law leads to the same result for the power law. Thus both forms of von Neumann's law predict asymptotic linear scaling of the froth. Inversely, if the constant κ changes in time, the observed growth rate will not be linear in time.

The observation of anomalously low growth exponents is common in metals, where initially well-dispersed impurities gradually segregate to the grain boundaries and reduce boundary mobility and hence slow (or even stop) grain growth. Inversely, the presence of impurities which increase boundary mobility results in growth exponents larger than 1.[11] In a froth the equivalent to a decreased boundary mobility is a decreased effective diffusion constant κ. Our previous measurement showed that κ stayed constant to within 5% over reasonably long times.[6] However, we did not measure κ at very long times when the exponent deviation was significant.[12] We have therefore looked more closely at possible causes of time-dependent diffusion constants.

We do not observe any difference in exponent between experiments done using helium and air, even though the helium bubbles evolve five times more rapidly, so changes

in the permeability of the soap films due to changes in their chemical structure as they age, are improbable. It seems more likely that any decrease in the diffusion constant is due to an increase in the amount of fluid per unit length of soap film in the sealed cell as bubbles disappear and the total length of bubble wall decreases. The diffusion constant is proportional to the product of the vertical extent of the thin film with the permeability of the thin film. A change in wall length can change both of these terms.

Since the fluid volume is very small, the excess fluid tends to accumulate in *Plateau borders,* which are triangular regions that appear wetting the top and bottom plates and also at the vertical intersections between three films. The borders are very thick compared to the actual soap films and effectively block the diffusion of gas across them. The typical width of the borders can be comparable to the separation between the top and bottom plates in the cell, and the borders can double in width during an experimental run, which means that the width increase can reduce substantially the unobstructed height of the soap films, and hence the total area of film available for diffusion. Thus the obstruction caused by broader borders results in a lower effective diffusion constant.

An alternative explanation would be that the soap films thicken as excess fluid accumulates. Even a small increase in film thickness would result in a decrease in the permeability of the soap films, and hence in the diffusion constant. We have no techniques to measure the film thickness during the experiment. However, we expect film thickness, if it increases at all, to increase with the amount of excess fluid available and hence with the width of the Plateau boarders. Measuring the dependence of the coarsening rate on the Plateau border width therefore measures an aggregate of obstruction and film-thickening effects.

We can measure only the widths of the borders and must estimate their vertical extent. In our calculations we assume that the vertical height of a Plateau border is one half its horizontal width, which is consistent with our observation of films at the borders of the cell. A larger wetting angle would result in a relatively larger obstructed area and hence in an effect of greater magnitude.

An additional complication is that images produced by our Mita Model DC-1255 photocopier are anisotropic. When we magnify the photocopies to measure the widths of the bubble walls some wall orientations produce smooth well-defined lines and some irregular lines with great variations in linewidth. Direct examination of an actual froth with a magnifying glass shows that this is an artifact and not a wetting effect of the Plexiglas. We therefore measure only lines oriented within 30° of that axis, which gives the smoothest line profiles, and average many measurements distributed over the entire pattern to reduce any remaining spatial anisotropy and measurement error. The uncertainty in the widths is approximately 25% of the measured values.

We present results for two air runs with different total fluid volumes in the same $\frac{1}{8}$-in.-thick cell in Fig. 3. In the first run the width of the Plateau borders increases approximately 50% during the experiment, and the fraction

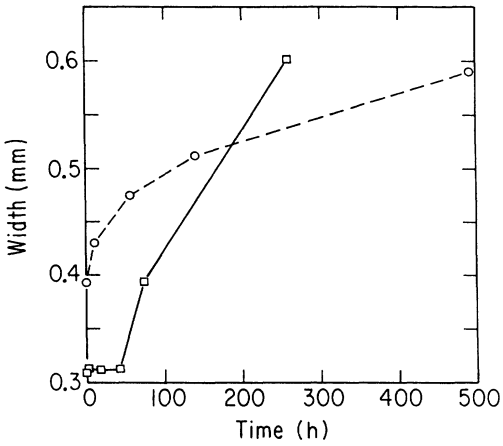

FIG. 3. *Plateau border broadening.* Plateau border widths vs time for two air runs. Run 1 (circles). Run 2 (squares).

of the film obstructed by the Plateau borders ranges from approximately 12.4% at the beginning of the run to 18.7% at the end. The growth exponent for this run is $\alpha=0.81$. The Plateau border width in the second run does not increase significantly until the number of bubbles decreases to fewer than 200 when the width doubles. The obstructed fraction grows from 9.9% at the beginning of the run to 19.0% at the end. The exponent for this run is $\alpha=0.50$.[6] The fact that a lower exponent corresponds to a larger percentage increase in obstructed area is strong evidence that a reduced diffusion constant is responsible for the changed exponent. As expected, the run with the initially larger Plateau border width evolves more slowly. We also obtain a larger exponent if we work in a larger cell in which film thickening is less important.[13]

We can begin to separate film-thickening effects from those of obstruction by repeating the experiment in cells with different heights. The effect of obstruction depends on the ratio between border height and cell height, and should be larger in a thinner cell. Film thickening depends on the absolute width of the Plateau borders and should be independent of cell thickness. Experimentally we find that cells with a thickness of $\frac{1}{8}$ in. have a larger average exponent ($\alpha=0.71\pm0.12$) than cells with a thickness of $\frac{1}{16}$ in. ($\alpha=0.58\pm0.12$), which suggests that Plateau border broadening dominates. However, since we have not controlled for total fluid volume the result is only indicative.

To obtain a definitive measure of the growth exponent in the soap froth, we need to repeat the grain growth measurement in a drained cell where the width of the Plateau borders, and hence the film thickness, is held constant.

Summarizing, we have calculated the generalized von Neumann's law using experimentally determined average internal angles in the two-dimensional soap froth. While the data agree slightly better with the modified form of von Neumann's law, both modified and unmodified laws are within our experimental error. We do not understand why the angle deviations should yield a nearly linear

modified growth law.

We believe that the reduction in film height available for diffusion caused by broadening of the Plateau borders as fluid accumulates in our sealed experimental cell (possibly augmented by film-thickening effects) can explain our previous observation of reduced growth exponents in the two-dimensional froth.

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