

SCALING IN THREE-DIMENSIONAL FOAMS

D.J. DURIAN*†, D.A. WEITZ†, AND D.J. PINE†

**Department of Physics, University of California, Los Angeles, CA 90024*

†*Exxon Research and Engineering Company, Rt. 22 E, Annandale, NJ 08801*

ABSTRACT

The coarsening and internal dynamics of a bulk foam are probed noninvasively by exploiting the strong multiple scattering of light that gives foams their familiar white color. By approximating the light propagation as a diffusion process, transmission measurements provide a direct probe of the average bubble size d . A second corroborating measure of d is obtained by analyzing temporal intensity fluctuations of the multiply scattered light within the framework of diffusing-wave spectroscopy. Both sets of measurements show the same behavior: At early times d is approximately a constant ($20\mu\text{m}$). After about twenty minutes the foam begins to coarsen and scaling behavior is observed such that the growth of d is a power-law in time, t^z with $z=0.45\pm 0.05$. This result is in near accord with the theoretical prediction, $z=1/2$, for foam in the limiting case of space-filling polyhedral bubbles. In addition, the change in packing conditions during coarsening gives rise to a nonequilibrium dynamical process which also exhibits temporal scaling: Neighboring bubbles undergo sudden structural rearrangements at a rate per unit volume which decays as $t^{-\gamma}$ with $\gamma=2.0\pm 0.2$. This value of γ cannot be explained by the presence of only a single time-dependent length scale in the foam structure. Since these bubble rearrangement events serve to relax local stress, they must also play a role in the relaxation of externally imposed stress. Therefore, elucidation of their origin and scaling behavior will lead to an increased understanding of the rheology and stability of foams.

INTRODUCTION

Foams are cellular materials which consist of a random dispersion of gas bubbles in a small volume fraction of liquid¹. They have a wide variety of uses based on their low density, high interfacial surface area, and their unusual rheological properties. In all such applications, however, the useful lifetime of the foam is limited since all foams are unstable and tend to coarsen over time. Scientifically, foams remain of current interest in part because neither the fundamental origin of their unique rheological behavior nor the physical mechanisms which affect their stability are well understood². Experimental study of such questions has traditionally been hampered by lack of direct, noninvasive probes of foam structure and dynamics. Since foams are intrinsically opaque, all attempts to optically image foam structure have previously been restricted to surface bubbles.

In this report, we exploit the strong multiple light scattering character of foams to develop quantitative probes of both the structure and internal dynamics of foam. We use these new techniques follow the time evolution of a three dimensional foam which coarsens by diffusion of gas from smaller to larger

bubbles. Power-law behavior is observed in the growth of the average bubble diameter and the decay of the rate of dynamic topological changes, suggesting that these features can be understood in terms of material-independent scaling arguments. The key points of the light scattering techniques³ and the scaling behavior⁴ have been described previously. The purpose of this report, then, is to summarize earlier results and present other significant details omitted from previous accounts.

SAMPLE PREPARATION

For convenient and reproducible foam samples, we used a commercial brand of shaving cream, Gillette Foamy Regular. This product makes use of the so-called three-phase aerosol technique to produce foam⁵. A surfactant solution and liquidified propellant are sealed into a metal container sufficiently strong to withstand the vapor pressure of the propellant. The propellant is only partially soluble in the surfactant solution and hence must be mechanically dispersed by shaking prior to use. When the emulsified product is released to atmospheric pressure, the propellant droplets evaporate and expand into bubbles, surfactants adsorb to the new liquid-vapor interfaces, and a foam is born. In Foamy, as in most shaving

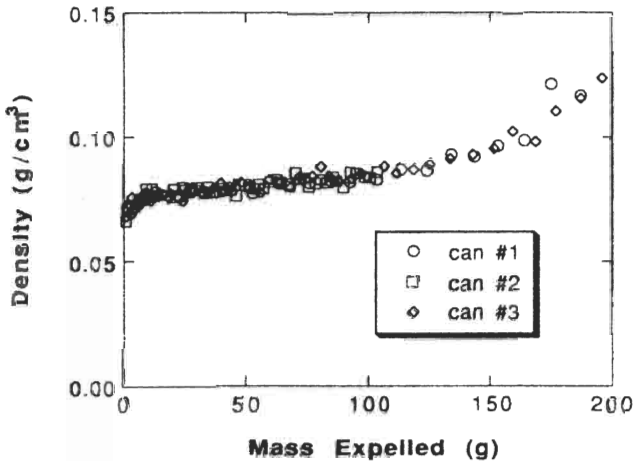


FIGURE 1 Foam density versus quantity previously expelled from the aerosol can. Results are shown for three different cans of Gillette Foamy Regular.

creams, the surfactant solution is stearic acid and triethanolamine in water; the propellant is a mixture of low molecular weight hydrocarbon gases chosen to have a particular vapor pressure. The reproducibility of the foam product is demonstrated by Figure 1, which shows the foam density as a function of how much foam has previously been expelled from the same can for three different cans. To within the accuracy of our measurements, all three cans produce foam with identical density: the first foam expelled is the least dense, and as more is expelled it becomes progressively wetter and more dense. The first 10-50 g expelled, however, has roughly a constant density of 0.077g/cm^3 ; all foam samples used in our experiments are taken from this region.

MULTIPLE LIGHT SCATTERING TECHNIQUES

Three different types of light scattering measurements are performed on such foam samples sealed into rectangular glass cells of known thickness. One side of the cell is illuminated with a plane wave of laser light with wavelength 488.0nm. We measure T , the fraction of light transmitted through the sample, and $g_1(\tau)$, the normalized electric field correlation function for the transmitted and the backscattered light. The $g_1(\tau)$ are obtained from the temporal fluctuations in the scattered intensity, and are analyzed within the framework of diffusing-wave spectroscopy (DWS)⁶. For backscattered light, $g_1(\tau)$ is nearly exponential in $\sqrt{\tau}$ with a time constant τ_0 defined by $g_1(\tau) = \exp(-2\sqrt{6\tau/\tau_0})$. For transmitted light,

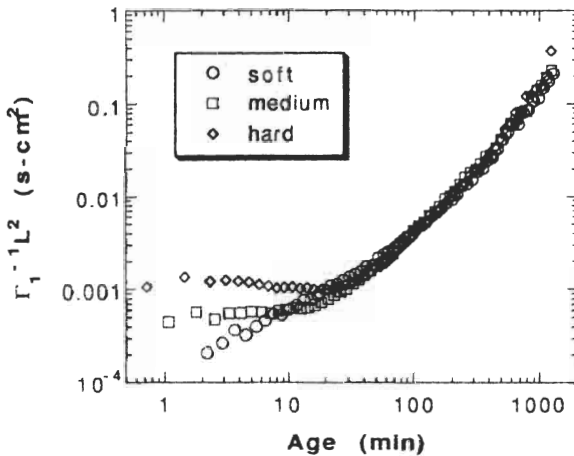


FIGURE 2 $\Gamma_1^{-1}L^2$ versus foam age for three different experimental runs which differ only in the rate at which foam was flowed into the cell at time zero. The first cumulant, Γ_1 , is defined in the text, and the cell thickness is $L=0.7\text{cm}$.

sets to perform valuable checks on our data collection and analysis procedures. It also is an indication that foam system reaches a scaling state, as discussed later.

To interpret our light scattering data in terms of the underlying foam structure and dynamics, we exploit the diffusive nature of light propagation inside the foam³. Physically, incident photons travel on average one transport mean free path l^* before sufficient scattering from liquid-vapor interfaces causes them to lose memory of their initial direction and commence a random walk of step size l^* . The value of l^* is determined by the foam structure and directly reflects the average bubble diameter d . For our samples, $l^* = (3.5 \pm 0.5)d$ and is consistent with a geometric optics picture of light reflecting or refracting from randomly oriented gas-liquid interfaces such that passage through several

$g_1(\tau)$ is nearly exponential in τ with a first cumulant Γ_1 defined by the small- τ behavior $-\ln(g_1(\tau)) = \Gamma_1\tau$. The time evolution of the first cumulant for transmission through a cell of thickness $L=0.7\text{cm}$ is shown in Figure 2 for three separate experimental runs. At time zero, foam was expelled into the cell at a different flow rate for each run. Figure 2 shows that while the initial behavior of $\Gamma_1^{-1}L^2$ can be varied by up to a factor of ten depending on the flow rate, the behavior after about twenty minutes is independent of initial conditions. This is very significant because it allows us to compare and combine different data

bubbles is required for full randomization of the light propagation³. An estimate of l^* , and hence the average bubble diameter d , can be determined directly from the static transmission data. In the limit of $L \gg l^*$ and no absorption, $T=5l^*/3L$. A second corroborating estimate can be made from the the two dynamic light scattering measurements: in the limit of $L \gg l^*$ and no absorption, the theory of DWS predicts $\Gamma_1^{-1}L^2=\tau_0 l^{*2}$. The expressions actually used to analyze our data account for the effects of absorption and finite L/l^* by expansion in the small dimensionless numbers $\alpha=l^*/L$ and $\beta=\sqrt{3L^2/l^*l_a}$:

$$T \approx \frac{(\delta + \frac{2}{3})\alpha\beta}{(1 + \frac{4}{3}\alpha)\sinh\beta} \quad (1)$$

$$\frac{\tau_0 l^{*2}}{\Gamma_1^{-1}L^2} = \frac{1 + 4\alpha + (\frac{8}{3}A)\alpha^2 - \frac{4}{3}A\alpha^3}{1 + \frac{4}{3}\alpha} - (1 + \frac{16}{3}\alpha + \frac{32}{3}\alpha^2 - \frac{64}{27}\alpha^3)\frac{\beta^4}{15} \quad (2)$$

In these expressions, $\delta=z_0/l^*$ and $A=(2\delta^2+\delta^3)/(\frac{2}{3}+\delta)$, where z_0 is the distance into the sample at which diffusing photons are assumed to be introduced. This point-source approximation, and other approximations in the boundary conditions for diffusing light, are discussed in detail in Reference 6. Here we take $\delta=1$, and hence $A=9/5$, since z_0 must clearly be on the order of l^* . Note that the parameter β represents the square root of the length of the characteristic diffusive light path through a sample of thickness L to the absorption length l_a . For our foam,³ $l_a=200\text{cm}$.

SCALING BEHAVIOR

In Figure 3 we plot the two independent estimates of d ; one is based on static transmission through cells of thickness $L=0.4, 0.7$, and 1.0cm ; the other is based on dynamic backscattering from a cell of thickness $L=1.0\text{cm}$ combined with dynamic transmission through cells of thickness $L=0.3, 0.4, 0.7$, and 1.0cm . The two data sets shown in Figure 3 exhibit identical behavior: At early times, when the effects of initial conditions still exist, the average bubble diameter is roughly constant. After twenty minutes, when no further effects of the initial conditions remain, scaling behavior is observed, with the average bubble diameter growing with time as a power-law t^z with $z=0.45 \pm 0.05$. By contrast with recent work where scaling behavior is observed in two-dimensional froth-like systems⁷, our work provides an experimental measurement of the scaling behavior and the growth exponent in a truly three-dimensional foam. Our experimental result is consistent with the theoretical prediction⁸ of $z=1/2$ for a dry foam of space-filling polyhedral bubbles. We speculate that our results seems to fall somewhat below $z=1/2$ due to the nonzero liquid content of our foam⁴. Instead of space-filling polyhedral bubbles, our foam is composed of closely packed, nearly spherical

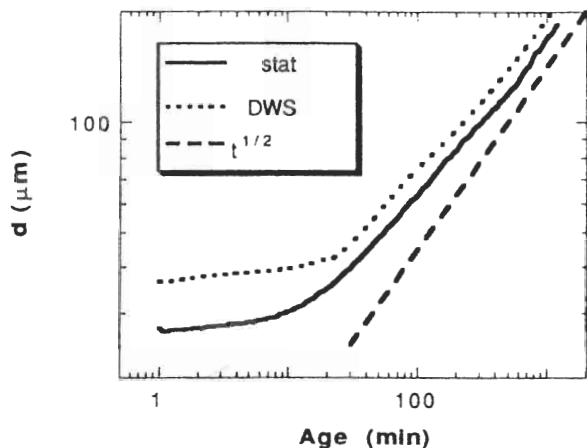


FIGURE 3 Average bubble diameter versus foam age as determined from two independent sets of multiple light scattering measurements. The first (stat) is from static transmission; the second is from combining diffusing-wave spectroscopy (DWS) measurements in transmission and backscattering geometries. The dashed line has slope $1/2$ and represents the predicted behavior in the limiting case of space-filling polyhedral bubbles.

are not free to adjust their positions due to their close packing. Thus stresses build as bubble shapes deform, until a threshold is reached and a rearrangement event occurs. These events can be thought of as a series of so-called⁹ "T1" neighbor-switching processes. A similar phenomenon has recently been observed in computer simulations of two-dimensional foams, where the effect of a single T1 process on the froth structure was found to cause a very long, but finite, range perturbation on the surrounding foam structure¹⁰.

The rate R of rearrangement events occurring per unit volume in our foam can be obtained from the dynamic light scattering data using a model of diffusing-wave spectroscopy which correctly predicts the full functional form of the observed $g_1(\tau)$ in both transmission and backscattering³. We find that the average time between rearrangements at a single location inside the foam is the same time measured directly in backscattering: $\tau_0 = 1/Rr^3$ where r is the spatial extent of the average rearrangement; for our foam³ $r = 10d$. Thus, from knowledge of Γ_1 and the average bubble diameter, we can determine the time evolution of R as shown in Figure 4. Again we observe scaling behavior: after about twenty minutes, R decreases as a power-law $t^{-\gamma}$ with $\gamma = 2.0 \pm 0.2$.

To the best of our knowledge, scaling behavior in the evolution of dynamical topological processes inside foam had not previously been suspected, let alone observed. There are, therefore, no theoretical predictions for the value

bubbles. Thus, the concentration profile of diffusing gas in the liquid film between neighboring bubbles is not strictly one-dimensional and the effect of the thick Plateau borders should be considered.

Additional evidence for scaling behavior in our foam is obtained from the time evolution of the internal dynamics as probed by temporal intensity fluctuations⁴. These fluctuations are caused by localized rearrangement events in which several neighboring bubbles move by a large fraction of their diameter³. As the foam coarsens, the packing conditions change but the bubbles

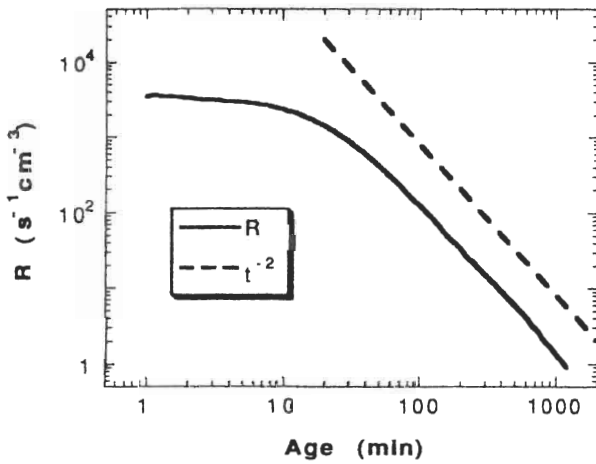


FIGURE 4 Rate of rearrangement events per unit volume vs foam age. The dashed line has slope -2 and shows that there is also scaling behavior in the internal dynamics of our foam system.

$$\frac{d(d/2)}{dt} \tau_0 = 50\text{nm}. \quad (3)$$

The magnitude of this new length scale, its origin, and its relationship to the physical mechanisms responsible for the rearrangement events are all, as yet, unresolved.

CONCLUSION

We have developed multiple light scattering techniques which directly and noninvasively probe both the structure and dynamics of bulk three dimensional foam. This allowed us to overcome the traditional problem of visualizing an opaque material and follow the time evolution of a particular, well defined, foam sample. We observed scaling behavior in the growth of the average bubble diameter, and in the decrease in the rate of sudden dynamic topological changes. These results are significant in indicating that much of foam behavior may be determined by the presence of only one, or perhaps two, important length scales in foam's structure. The light scattering techniques themselves are of sufficient generality and simplicity that a wide variety of other foams and emulsions can also be investigated and characterized noninvasively. This may lead to better knowledge of the fundamental mechanisms controlling foam rheology and stability.

of y with which we may compare our data. No doubt, a prediction of the correct value of y must ultimately rely on a better understanding of the physical mechanisms which lead to rearrangement events. It is perhaps surprising and significant that our data suggest the presence of a second important length scale in the foam structure. According to our results for y and z , the average distance a bubble wall moves in the time τ_0 between rearrangements scales as time raised to the power $y-2z-1 \approx 0$, and is hence a constant independent of time:

REFERENCES

1. See, e.g., J.J. Bikerman, *Foams* (Springer-Verlag, New York, 1973); J.H. Aubert, A.M. Kraynik, P.B. Rand, *Sci. Am.* **254**, 74 (May 1986); or A.J. Wilson, ed., *Foams: Physics, Chemistry, and Structure* (Springer-Verlag, New York, 1989).
2. A.M. Kraynik, *Ann. Rev. Fluid Mech.* **20**, 325 (1988).
3. D.J. Durian, D.A. Weitz, D.J. Pine, *Science* **252**, 686 (1991).
4. D.J. Durian, D.A. Weitz, D.J. Pine, to appear in *Phys. Rev. A*, (1991).
5. P.A. Sanders, *Handbook of Aerosol Technology*, second edition (Van Nostrand, New York, 1979).
6. D.J. Pine, D.A. Weitz, J.X. Zhu, E. Herbolzheimer, *J. Phys. (Paris)* **51**, 2101 (1990).
7. J.A. Glazier, S.P. Gross, and J. Stavans, *Phys. Rev. A*, **36** 306 (1987); K.J. Stine, S.A. Rauseo, B.G. Moore, J.A. Wise, and C.M. Knobler, *Phys. Rev. A*, **41** 6884 (1990); B. Berge, A.J. Simon, and A. Libchaber, *Phys. Rev. A*, **41** 6893 (1990); J. Stavans, *Phys. Rev. A*, **42** 5049 (1991).
8. W.W. Mullins, *J. Appl. Phys.* **59**, 1341 (1986).
9. D. Weaire and N. Rivier, *Contemp. Phys.* **25**, 59 (1984).
10. T. Herdtle and H. Aref, preprint (1991).