PHYSICAL REVIEW E VOLUME 57, NUMBER 6 JUNE 1998

# Viscoelastic response of a coarsening foam

Sylvie Cohen-Addad,* Hussein Hoballah, and Reinhard Höhler†
*Laboratoire de Physique des Matériaux Divisés, Université de Marne-la-Vallée, 5 Boulevard Descartes, Champs-sur-Marne,*
*77454 Marne-la-Vallée Cedex 2, France*

(Received 4 August 1997; revised manuscript received 23 January 1998)

We have investigated the influence of the coarsening process on the complex shear modulus of three-dimensional aqueous foam. It is shown that the viscoelastic response is governed by a large spectrum of relaxation times and that the complex shear moduli measured as a function of frequency, at different foam ages, can be superposed on a single master curve using a scaling law. These results are in agreement with the hypothesis that aqueous foam can be modeled as an elastic matrix in which isotropic weak regions are dispersed. We find that the relaxation times associated with all of these weak regions must increase with foam age according to a parabolic law. [S1063-651X(98)08006-4]

PACS number(s): 82.70.Rr, 83.70.Hq

## I. INTRODUCTION

Concentrated dispersions of gas bubbles in a surfactant solution never settle into an equilibrium. Their structure evolves with time due to interbubble gas diffusion, liquid drainage, and bubble coalescence. The relative importance of these mechanisms strongly depends on the physical and chemical characteristics of the foam. When gas diffusion driven by the Laplace pressure is dominant, the structure undergoes a coarsening process [1,2]. Although the foams considered here are only constituted of fluids, they behave like viscoelastic solids when they are subjected to a small stress. Beyond a yield stress, a Bingham plastic behavior is observed. These rheological properties of aqueous foams have been the subject of previous experimental investigations [3–5]. Khan studied the complex shear modulus of freshly formed foams as a function of frequency in small-amplitude oscillatory experiments [3]. He showed that both the elastic and loss moduli, which we call $G'$ and $G''$, remain nearly constant in the range of frequencies 0.06–1.6 Hz, suggesting a large spectrum of relaxation times. Similar behavior at very low frequencies has been observed in recent rheological experiments on concentrated emulsions [6–8]. To explain these features, theoretical models describing the rheology of soft glassy materials, such as emulsions or foams, have recently been proposed [9–12].

In this paper we study the influence of the coarsening process on the viscoelastic behavior of a three-dimensional, disordered, wet gas-liquid foam, well below the yield stress. As the mean bubble size increases, the static as well as the dynamic rheological properties evolve with time. We show that the frequency dependence of the complex shear modulus undergoes pronounced changes as the foam coarsens and that this evolution is governed by a scaling law. Moreover, in strongly coarsened foam, the loss modulus grows as $\omega^{0.5}$ at high angular frequency $\omega$, in qualitative agreement with a theoretical prediction [12].

## II. EXPERIMENT

The foam samples used in the experiments consist of a commercial so-called aerosol-generated shaving cream [13]. During the whole duration of the experiments, drainage and coalescence are not significant and we consider that the foam structure evolves with time solely because of interbubble gas diffusion. The gas volume fraction $\phi$ was measured as a function of foam age, i.e., the time elapsed since the production of the sample. Initially $\phi$ is equal to $(92.6\pm 0.4)\%$ and it increases slightly to reach $(93.6\pm 0.4)\%$, 8 h after foam production [2]. Visual observations of the bubbles located near the surface of the sample show that 15 min after foam production, the mean bubble radius is equal to 12 $\mu$m and that 8 h later, it reaches 50 $\mu$m. During this time, the shape of the bubbles remains nearly spherical and the dimensionless second moment of the bubble size distribution remains constant at a value of $0.60\pm 0.05$.

The rheological measurements were performed using a controlled stress rheometer (Carry-med CSL 100) with a Couette configuration. To prevent wall slip, the cylinder surfaces were roughened. After this treatment, the effective gap width was determined using a silicone oil of known viscosity. The radius of the inner cylinder was 12.5 mm and the effective gap width could be set to either 3.3 or 5.3 mm. The efficiency of the surface treatment was controlled by performing a creep experiment as described in detail elsewhere [2]. Additional proof for the absence of wall slip is provided by the fact that the measured complex shear modulus is independent of the gap width. In order to prevent evaporation, the sample cell was saturated with humidity. The temperature was regulated to $(20.5\pm 0.5)$°C using a water bath surrounding the Couette cell.

The experiments consisted in applying to the sample a sinusoidal shear stress of an amplitude equal to either 0.1 or 1 Pa and in measuring the resulting deformation to obtain the complex shear modulus $G^*$. The frequency of the mechanical oscillation was varied between 0.04 and 3 Hz. These experiments were performed at foam ages ranging from 15 min to 8 h. Between successive measurements the sample was not sheared. Furthermore, we have subjected foam samples to slowly increasing shear stress ($0.25\ \mathrm{Pa\,s^{-1}}$) and

---

*Electronic address: Sylvie.Cohen-Addad@univ-mlv.fr
†Electronic address: Hohler@univ-mlv.fr

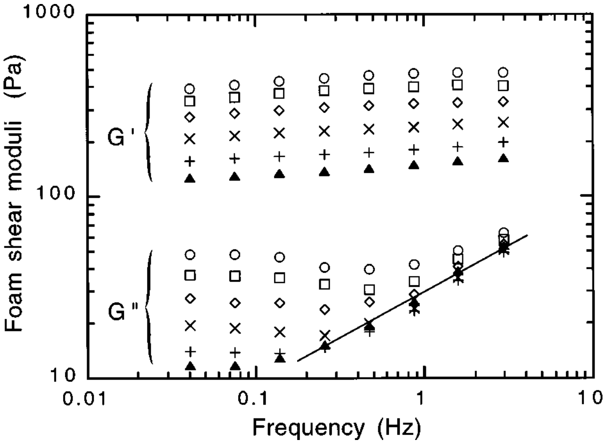

FIG. 1. Storage and loss moduli $G'$ and $G''$ of coarsening foam plotted versus frequency. The sample is subjected to an oscillating shear stress with an amplitude of 1 Pa. Measurements at different foam ages are labeled as follows: 15 min, circles; 30 min, squares; 1 h, diamonds; 2 h, crosses; 4 h, pluses; and 8 h, triangles. The continuous line has a slope of $\frac{1}{2}$ and shows the power-law behavior of $G''$ at high frequency and foam age.

measured the shear strain rate for foam ages ranging from 15 min to 8 h.

## III. RESULTS

Figure 1 shows the frequency dependence of the storage and loss shear moduli $G'$ and $G''$ at different foam ages. We observe that, for a given age, $G'$ is a slightly increasing function of frequency $f$, reflecting the viscoelastic response of the material. Our measurements of $G'$ are in good agreement with those obtained earlier on freshly formed foams with gas volume fractions and bubble sizes comparable to those of our samples [3]. The frequency dependence of $G''$ is more complex than that of $G'$. For a given foam age, there is a plateau at low frequencies, in qualitative agreement with previous results obtained using young foams [3]. As $f$ increases, a shallow minimum appears, and at still higher frequencies, $G''$ strongly increases. These results do not depend significantly on the amplitude of the applied stress in the investigated range between 0.1 and 1 Pa. This can be seen in Fig. 2, where the time evolutions of $G'$ and $G''$ for different stress amplitudes are shown for two fixed frequencies. Furthermore, for each age, the yield stress can be estimated by extrapolating the stress versus shear strain rate data to zero shear rate. As Fig. 3 shows, the yield stress always remains far above 1 Pa. Indeed, at applied stresses of 1 and 0.1 Pa, the measured shear strain rate was equal to zero within experimental resolution, whatever the investigated foam age. These results show that the measurements of $G'$ and $G''$ described above were carried out in the linear viscoelastic regime.

Let us note that the kind of viscoelastic response shown in Fig. 1 has been observed for other complex fluids such as concentrated monodisperse emulsions [6–8]. Lyotropic lamellar systems in the onion phase also exhibit the same type of behavior [14]. The apparent generality of this viscoelastic behavior has motivated the speculation that it may be due to a common basic mechanism [11]. In contrast to the other materials just mentioned, the structure of foam evolves with time due to a coarsening process: The interbubble gas diffusion leads to an increase of the mean bubble size, which in turn yields a decrease of the specific surface and thus of $G'$. This softening effect is indeed observed in Fig. 1 and has been studied in detail elsewhere [2]. Concerning the loss modulus, Fig. 1 shows that the basic pattern of a plateau followed by a shallow minimum and a steep rise persists as foam age increases. However, these features are systemati-

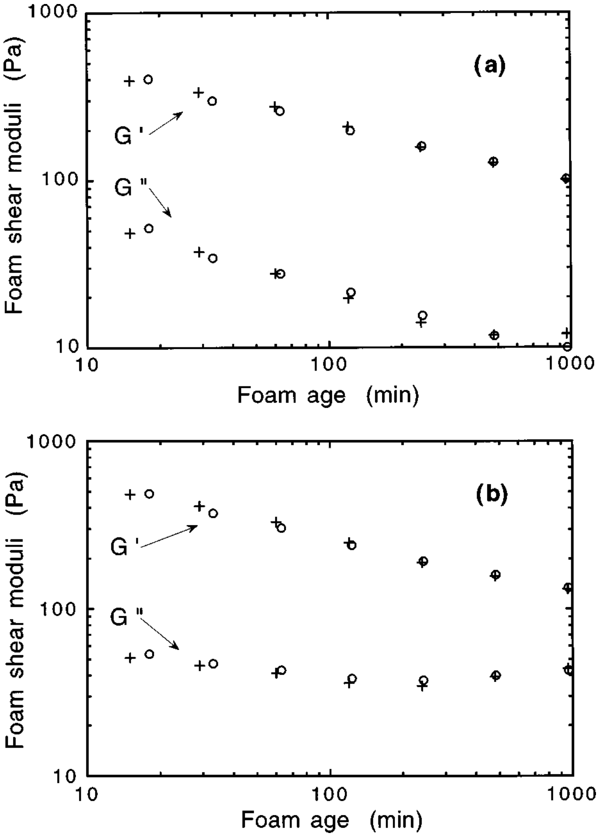

FIG. 2. Temporal evolution of the storage and loss moduli plotted for applied stress amplitudes of 0.1 Pa (circles) and 1 Pa (crosses). The frequency of the oscillating shear stress is equal to (a) 0.04 Hz and (b) 1.6 Hz.

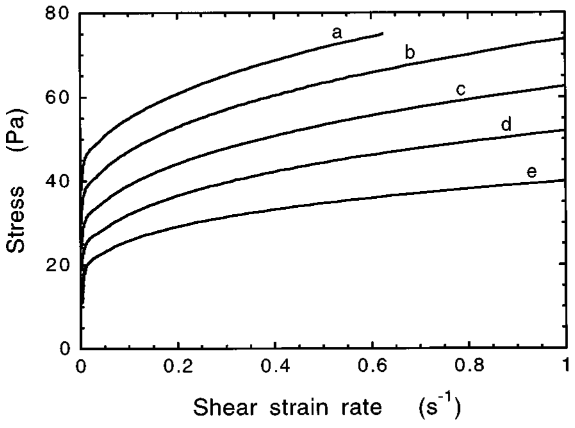

FIG. 3. Stress versus shear strain rate. The sample is subjected to slowly increasing shear stress. Measurements were performed at different foam ages, corresponding to the following labels: $a$, 15 min; $b$, 30 min; $c$, 1 h; $d$, 2 h; and $e$, 8 h.

cally shifted towards lower frequencies. At high frequency, an asymptotic dependence $G''(f) \propto f^{1/2}$ emerges more and more clearly with increasing foam age. As shown in Fig. 1, the data obtained at the most advanced age exhibit this power-law behavior over one decade. Such a dependence at high frequency has been predicted theoretically [12] and observed in concentrated emulsions [6–8].

## IV. DISCUSSION

Before discussing our results, let us briefly recall some features of an aqueous foam that coarsens due to interbubble gas diffusion. Numerical simulations [15] as well as experimental work [1,2] have shown that in this case, the foam rapidly reaches a scaling state. This means that the aging of the foam structure is governed by the time evolution of a single characteristic length scale, which can be chosen as the first moment of the bubble radius distribution $R_1(t)$. Furthermore, it has been shown theoretically and experimentally that $R_1(t)$ increases with foam age according to a parabolic law of the form $R_1^2(t) - R_1^2(t_0) \propto t - t_0$, where $t_0$ is an arbitrary reference time [1,2,16]. To describe the static mechanical shear modulus $G_0$ of foam, Princen and Kiss have proposed a semiempirical model relating the shear modulus to the second and third moments of the bubble radius distribution $R_2$ and $R_3$ [17]:

$$G_0 = 1.8\gamma(\phi - \phi_c)\phi^{1/3}\frac{R_2}{R_3}, \tag{1}$$

where $\gamma$ is the foaming solution surface tension and $\phi$ the gas volume fraction. We have recently determined $\phi_c = 0.66$ [18]. As the mean bubble size increases with time, $G_0$ becomes smaller and the foam gets softer. When the foam is in the scaling state as mentioned above, it can be shown that $G_0$ decreases as $1/R_1(t)$ provided the evolution of $\phi$ is taken into account [2]. To summarize, in the Princen-Kiss model, foam is described at a macroscopic level as a purely elastic medium characterized by an average shear modulus. This physical picture must be refined in order to describe the observed viscoelastic response.

At the scale of the liquid lamellae separating bubbles, mechanical relaxations may be due to viscous flows and surface rheological phenomena [9,10]. Neglecting the second effect, Durian has estimated the characteristic time after which individual bubbles relax towards a local mechanical equilibrium: $\tau_d \propto \eta R_1^2/\gamma d$ [19]. $\eta$ is the foaming solution viscosity and $d$ is the thickness of films between neighboring bubbles. To obtain the order of magnitude of $\tau_d$, we suppose that $\eta$ is the viscosity of water, $d$ is of order 1 $\mu$m, $\gamma$ is of order 30 mN/m, and $R_1$ is equal to 30 $\mu$m, which is the mean bubble radius in our samples at a foam age of 3 h. This yields $\tau_d \propto 10^{-5}$ s, which is much shorter than our experimental time scale. Thus individual bubble motions cannot explain the relaxations we observe. Recent numerical simulations have shown that collective bubble motions can have relaxation times many orders of magnitude larger than $\tau_d$ [19,20].

Recently, two analytical models have been proposed to describe the origin of the relaxation modes in concentrated emulsions and foams. Both of them use a coarse-grained description where mesoscopic regions, with well-defined mechanical properties, are randomly distributed. In the model proposed by Sollich *et al.*, the mesoscopic regions are characterized by a local yield strain beyond which the neighboring bubbles rearrange in a new equilibrium configuration [11]. Interactions between such regions are represented by a mean-field ''noise temperature.'' According to this model, the dependence of $G''$ on frequency follows a power law and, for a certain value of the noise temperature, an exponent of $\frac{1}{2}$ is predicted. However, our loss modulus data cannot be described by a single power law in the entire investigated range of frequencies, at any given foam age. The future development of the model proposed by Sollich may show how this discrepancy can be interpreted. Liu *et al.* have elaborated a model in which local, randomly oriented planes of easy slip are the origin of an anomalous viscoelastic behavior. The neighborhoods of such planes are called weak regions; they are characterized by an anisotropic shear modulus [12]. In the framework of this model, the macroscopic complex shear modulus is obtained as the sum of three contributions. The first term arises from the matrix surrounding the weak regions whose elastic modulus is supposed to be frequency independent and real. The second term is due to the weak regions themselves; it is proportional to $(i\omega)^{1/2}$. It is only at frequencies $\omega$ higher than $\gamma/\eta R_1$ that conventional viscous loss, described by a third term, linear in $\omega$, becomes dominant. The anomalous dissipation predicted by Liu *et al.* is indeed observed in concentrated emulsions over several decades in frequency [6,8]. For our samples, the cross over towards a linear dependence of $G''$ on $\omega$ should occur for angular frequencies of the order of $10^6$ s$^{-1}$. Since our data were taken in the range 0.04–3 Hz, the loss modulus should increase as $\omega^{1/2}$. Indeed, our data seem to converge towards such a power law for the highest frequencies and foam ages. However, the behavior of $G''$ observed at low frequencies and foam ages does not follow the prediction. This might be due to additional slow relaxation modes, possibly arising from the coarsening process.

None of the published models describing the viscoelastic response of foam predict the following scaling property of the complex shear modulus $G^*$ that we have found by analyzing our experimental data. Let us choose $G''(\omega,t_0)$ measured at an age of $t_0 = 15$ min as a reference. All the other curves $G''(\omega,t)$ obtained at later times $t$ can be superposed onto this reference by multiplying the frequencies by a parameter $a(t,t_0)$ and dividing the moduli by another parameter $b(t,t_0)$. $a(t,t_0)$ and $b(t,t_0)$ are independent of the frequency. Applying the same procedure to $G'(\omega,t)$ and using exactly the same parameters $a(t,t_0)$ and $b(t,t_0)$ again gives rise to a master curve. Mathematically, this procedure may be written in the form

$$G^*(\omega,t) = b(t,t_0)G^*(\omega a(t,t_0),t_0). \tag{2}$$

As shown in Fig. 4, the loss and the storage moduli thus obey the same scaling law in the entire investigated ranges of foam age and frequency. Let us note that a scaling by the factor $b(t,t_0)$ alone, as suggested by the Princen-Kiss model and the time dependence of the mean bubble radius, does not lead to a master curve.

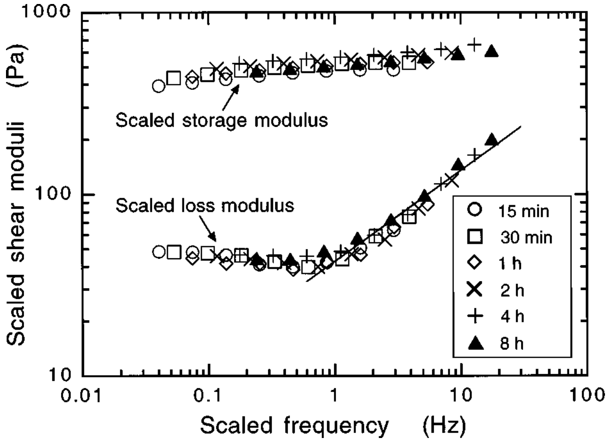

FIG. 4. Scaled moduli, obtained from the data of Fig. 1, represented versus the scaled frequency, as defined in the text, for foam ages ranging between 15 min and 8 h. The continuous line represents a power law of exponent $\frac{1}{2}$, fitted to the data at scaled frequencies above 2 Hz.

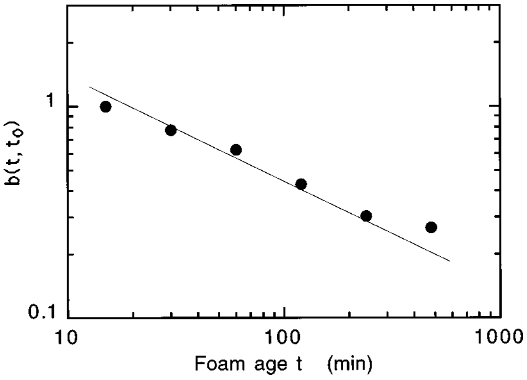

FIG. 5. Evolution of the shear modulus scaling factor $b(t,t_0)$ with foam age. The continuous line has slope $-\frac{1}{2}$, corresponding to a theoretical prediction.

To interpret our experimental results, we start from the basic idea suggested by the numerical simulations [19,20] that the dissipation occurs in soft, viscoelastic regions embedded in an isotropic elastic matrix. We assume that the matrix shear modulus $G_0(t)$ is described by the Princen-Kiss model and that $R_1(t)$ evolves with foam age $t$ according to the parabolic law described above. The weak regions are modeled as spherical isotropic viscoelastic inclusions that will be distinguished by an index $I$. In the absence of sufficient experimental information about local rheological properties, no restrictive hypothesis is made at this stage about the local loss moduli $i\omega\eta_I$. Concerning the local storage moduli $g_I$ in the weak regions, we only suppose that they are small compared to $G_0(t)$. Let $\nu_I$ be the volume fraction occupied by inclusion $I$. Since, according to the scaling state picture, dimensionless structural characteristics are not modified by the coarsening process, $\nu_I$ should not evolve with foam age. Using some results of the theory of heterogeneous elastic materials, the macroscopic complex shear modulus is written [21]

$$G^*(\omega,t)=G_0(t)\,\frac{1+3M(\omega,t)/2}{1-M(\omega,t)}, \tag{3}$$

with

$$M(\omega,t)=2\sum_I \nu_I\,\frac{g_I+i\omega\eta_I-G_0(t)}{2(g_I+i\omega\eta_I)+3G_0(t)}. \tag{4}$$

In this calculation, the elastic interactions among the weak regions are taken into account by a mean-field approach. Since the shear moduli of the inclusions are supposed to be small compared to that of the matrix, we neglect them in the following. Furthermore, we introduce a characteristic relaxation time of the inclusions $\tau_I=\eta_I/G_0$. In this notation, we obtain

$$G^*(\omega,t)=G_0(t)\,\frac{1+3\sum\limits_I \nu_I\,\dfrac{i\omega\tau_I(t)-1}{2i\omega\tau_I(t)+3}}{1-2\sum\limits_I \nu_I\,\dfrac{i\omega\tau_I(t)-1}{2i\omega\tau_I(t)+3}}. \tag{5}$$

This expression is in agreement with the empirical scaling law (2) derived from our experimental data provided that the parameters $a(t,t_0)$ and $b(t,t_0)$ can be identified as

$$\frac{G_0(t)}{G_0(t_0)}\propto b(t,t_0), \tag{6}$$

$$\frac{\tau_I(t)}{\tau_I(t_0)}\propto a(t,t_0). \tag{7}$$

To discuss relation (6), let us recall that according to the Princen-Kiss model and the scaling state hypothesis, $G_0(t)/G_0(t_0)$ evolves asymptotically as one over the square root of the foam age if the gas volume fraction is constant. This is in good agreement with the experimentally obtained time evolution of $b(t,t_0)$ as can be seen in Fig. 5. The small deviation at the highest foam age can in part be explained by the slow increase of the gas volume fraction. Relation (7) implies that a common factor governs the increase of all the mechanical relaxation times $\tau_I$ with foam age. As illustrated

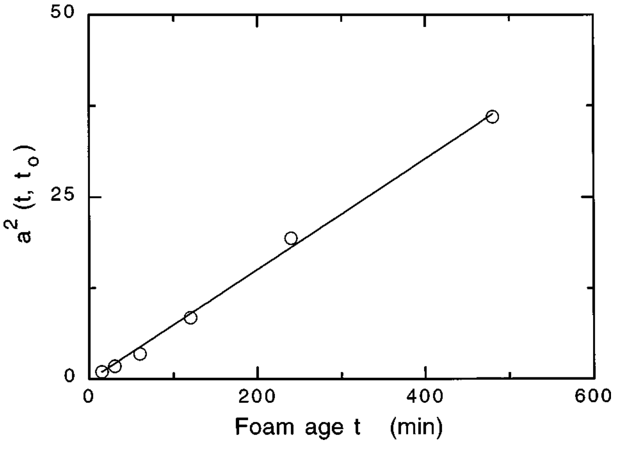

FIG. 6. Square of the frequency scaling factor $a(t,t_0)$ plotted as a function of foam age. The continuous line represents a linear fit.

in Fig. 6, the evolution of $a(t,t_0)$ is accurately described by a parabolic law of the form $a^2(t,t_0)-1\propto t-t_0$. Thus the evolution with foam age of the relaxation times $\tau_I$ is formally similar to that of the characteristic lengths describing the foam structure. Since $a(t,t_0)$ evolves as $1/G_0$, the viscosities $\eta_I$ do not seem to evolve with foam age.

## V. CONCLUSION

We have shown that the complex shear modulus of aqueous foam obeys a scaling law, as the foam evolves due to the coarsening process. By multiplying frequency and complex modulus by two different factors, scaled moduli at different foam ages can be obtained that form a single master curve. Based on the picture of weak viscoelastic inclusions dispersed in an elastic matrix, the Princen-Kiss model, the scaling state hypothesis, and a limited number of assumptions, we propose a simple model that reproduces this scaling property. The next step in the analysis will be to take into account anisotropic viscoelastic inclusions. This should provide a link between our model and the one proposed by Liu *et al.*, which predicts the square root of the $\omega$ dependence of $G''(\omega)$ observed at high frequency. Furthermore, the relation between the mechanical macroscopic relaxation at low frequencies and the rearrangement processes at the bubbles scale, as observed by diffusing-wave spectroscopy, is the subject of ongoing work.

## ACKNOWLEDGMENTS

We thank Pierre Mills for discussions. The rheological measurements were carried out at the Laboratoire Biorhéologie et Hydrodynamique Physique at Université Paris 7 and we express our gratitude towards Christophe Baravian for his help with the Carry-med rheometer. This work was financially supported by the Ministère de l'Enseignement Supérieur et de la Recherche through the Équipe d'Accueil 2179.

---

[1] D. J. Durian, D. A. Weitz, and D. J. Pine, Phys. Rev. A **44**, R7902 (1991).

[2] H. Hoballah, R. Höhler, and S. Cohen-Addad, J. Phys. II **7**, 1215 (1997).

[3] S. A. Khan, C. A. Schnepper, and R. C. Armstrong, J. Rheol. **32**, 69 (1988).

[4] R. K. Prud'homme and S. A. Khan, *Surfactant Science Series* (Dekker, New York, 1996), Vol. 57, p. 217.

[5] M. F. Coughlin, E. P. Ingenito, and D. Stamenovic, J. Colloid Interface Sci. **181**, 661 (1996).

[6] T. G. Mason and D. A. Weitz, Phys. Rev. Lett. **74**, 1250 (1995).

[7] T. G. Mason, J. Bibette, and D. A. Weitz, Phys. Rev. Lett. **75**, 2051 (1995).

[8] T. G. Mason, H. Gang, and D. A. Weitz, J. Opt. Soc. Am. A **14**, 139 (1997).

[9] Y. Hemar, R. Hocquart, and F. Lequeux, J. Phys. II **5**, 1567 (1995).

[10] D. M. A. Buzza, C.-Y. D. Lu, and M. E. Cates, J. Phys. II **5**, 37 (1995).

[11] P. Sollich, F. Lequeux, P. Hébraud, and M. E. Cates, Phys. Rev. Lett. **78**, 2020 (1997).

[12] A. J. Liu, S. Ramaswamy, T. G. Mason, H. Gang, and D. A. Weitz, Phys. Rev. Lett. **76**, 3017 (1996).

[13] The Gillette Company, Gillette UK Ltd., London.

[14] P. Panizza, D. Roux, V. Vuillaume, C.-Y. D. Lu, and M. E. Cates, Langmuir **12**, 248 (1996).

[15] M. P. Anderson, G. S. Grest, and D. J. Srolovitz, Philos. Mag. B **59**, 293 (1989).

[16] W. W. Mullins, J. Appl. Phys. **59**, 1341 (1986).

[17] H. M. Princen and A. D. Kiss, J. Colloid Interface Sci. **112**, 427 (1986).

[18] H. Hoballah, Ph.D. thesis, Université de Marne-la-Vallée (1998).

[19] D. J. Durian, Phys. Rev. Lett. **75**, 4780 (1995); Phys. Rev. E **55**, 1739 (1997).

[20] S. A. Langer and A. J. Liu, J. Phys. Chem. (to be published).

[21] J. F. Palierne, Rheol. Acta **29**, 204 (1990).