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Time Evolution of the Elastic Properties of Aqueous Foam

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Abstract. — We have measured the shear modulus of three-dimensional aqueous foam under a small oscillating stress. The foam structure has also been characterized by measurements of the optical transmission. Each of these physical properties depends on a characteristic length, related to the bubble size distribution. We have shown that both lengths follow the same evolution as a function of foam age. They grow according to a parabolic law, in agreement with theoretical predictions.

1. Introduction

Aqueous foams are highly concentrated dispersions of gas in a solution containing surfactants. They exhibit remarkable mechanical properties: under large stresses, they flow like a liquid whereas under small stresses they behave as a viscoelastic solid [1]. Many industrial applications such as oil recovery, fire fighting and the production of textiles take advantage of these properties [2]. Real foams are strongly disordered materials and it is only in recent years that some progress has been made toward an understanding of the basic mechanisms that govern their physical properties. Close analogies with apparently quite different systems have been discovered, in particular with other cellular materials: the temporal evolution of the foam structure is analogous to that of polycrystalline solids during annealing [3]. Furthermore, it has been conjectured that, unless compression is involved, the elastic properties of disordered foams and concentrated emulsions are very similar and can be described by a common model [4].

In this paper, we focus on the ageing of the foam structure which never settles in a static equilibrium. Driven by the Laplace pressure, gas diffuses from smaller to larger bubbles, giving rise to the shrinkage of small bubbles for the benefit of larger ones. This in turn yields growing strains that lead to rearrangements of the cells. The liquid in the foam is drained due to gravity and capillary pressure. Moreover, the films are subjected to thermal and mechanical fluctuations; thin lamellae become unstable and coalescence between neighbouring bubbles may occur. All of these processes determine how the physical properties of foam evolve with time. In the following, we restrict our study to foams whose coarsening is essentially due to gas diffusion. Using computer simulations [5, 6] or analytical arguments based on the conjecture

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that the foam structure is statistically self-similar [7], it has been predicted that the increase of the mean bubble size with foam age should converge to a power law with an exponent of 0.5. Indeed, measurements of the diffuse optical transmission and of the mean bubble size at the sample surface have shown that for a commercial shaving cream, the growth of the mean bubble size converges to a power law with an exponent equal to 0.45 ± 0.05 [8]. However, such a scaling behaviour has not been detected in a recent study of whipped gelatine foam by NMR imaging [9]. Unfortunately, this experimental technique is not adapted to the study of shaving cream so that a direct verification is not possible. In view of this debate, it is of interest to analyse different physical properties of shaving cream that depend on the bubble size distribution and thus provide additional evidence. In the following, we present new measurements of the dynamic shear modulus of shaving cream as a function of time. Identical samples were characterized by light transmission experiments. The prediction of the scaling state model is tested by comparing these two physical properties.

2. Foam Samples

Commercial shaving cream [10] was chosen because it is very stable. Moreover, the drainage of the liquid fraction is very slow and the bubbles do not coalesce on our experimental time scale [8]. In order to characterize the foam, its gas volume fraction, ϕ , was determined. A sample was injected into a cell whose height (7 cm) is close to the one of the cell in the rheometer. It was kept in an atmosphere saturated with moisture. At a given foam age, two volumes of foam (5 ml each) were taken from the sample at positions 1.5 cm and 5.5 cm above the bottom of the vessel, corresponding to the lower and upper limits of the sensitive region of the rheometer. The volume fractions, called respectively ϕ_l and ϕ_h , were measured by weighing. Such experiments were carried out for foam ages ranging from 10 to 1440 minutes. The experimental uncertainty of these measurements was $\pm 0.4\%$. ϕ_h and ϕ_l remain constant and equal to each other for the first 2 hours. At later times, ϕ_h and ϕ_l start growing, and ϕ_h increases slightly more rapidly than ϕ_l . Since the difference between ϕ_h and ϕ_l never exceeds 2%, we characterize the samples by the mean value of ϕ_h and ϕ_l , called ϕ . This simplification is pertinent in view of the accuracy necessary for the interpretation of the rheological experiments as we will discuss later. The data are reported in Table I. All of these measurements were performed at 21 ± 1 °C.

Table I. — *The gas volume fraction of foam sample ϕ is determined as a function of its age, i.e. the time elapsed since the foam production.*

Foam age (min)	ϕ
10	92.6
35	92.7
60	92.7
120	92.9
240	93.1
480	93.6
960	93.9
1440	94.7

3. Rheological Experiments

The measurements were taken using a controlled stress rheometer which has a Couette configuration (Carri-med CSL 100). The height of the cylinders was 28 mm. In order to eliminate wall slip, the inner cylinder was grooved (depth 0.5 mm), and sand with a grain diameter of $250 \pm 50 \mu\text{m}$ was glued onto the surface of the outer cylinder. Since this treatment modifies the gap between the cylinders in a non-uniform manner, we have performed calibration experiments using a silicone oil of known viscosity. For the two different outer cylinders used in the experiments, the effective gap was found to be equal to 3.3 mm and to 5.3 mm. To check whether the surface treatment was effective in preventing wall slip, the rheometer was filled with shaving cream and, during 25 seconds, a constant shear stress of 1 Pa was imposed, corresponding to the stress that was used in all of the later experiments. The induced deformation was measured during and after the application of stress. This test was performed with both gap widths. During all the experiments, the sample cell was surrounded by a water bath at a controlled temperature in the range 20–21 °C. In order to avoid evaporation, the cell was closed and the air inside saturated with moisture. The rheological experiments presented in the following consisted in subjecting the sample to an oscillating shear stress of an amplitude of 1 Pa and a frequency of either 0.04 Hz or 1.6 Hz. The real part of the shear modulus G' was obtained from the oscillation of the induced sample deformation. It was measured at logarithmically increasing time intervals, 10 to 1000 minutes after foam production. The foam was not sheared between measurements.

4. Optical Experiments

The foam structure was characterized using the technique of diffuse transmission spectroscopy which consists in measuring the intensity of light transmitted through an opaque medium [8,11]. The cell is rectangular (8 cm \times 6 cm), delimited by two transparent glass plates, hermetically sealed and it can be placed either vertically or horizontally. A sample thickness of 10 mm was chosen to ensure multiple scattering. The light source is a He-Ne laser (wavelength equal to 633 nm). The light transmitted in the direction perpendicular to the sample surface is detected with a photodiode. Since the angular distribution of transmitted light has been shown to be independent of the foam age [12], the detected signal is at all times t proportional to $T(t)$, the fraction of transmitted light. A chopper and a lock-in amplifier are used to raise the signal to noise ratio.

5. Theoretical Models

The time evolution of three-dimensional cellular structures has been studied by a great number of authors. These theoretical investigations involve computer simulations [5, 6] as well as different analytical calculations based on a statistical self-similarity conjecture [7] or topological arguments [13]. A recent review of this subject is available [3] and we will only recall some of the main results related to this paper. We focus on wet foams containing spherical polydispersed bubbles. Let us call r the radius of a bubble and $\rho(r, t)$ the normalized probability density of finding such a bubble, at time t . The moment of order n of the radius distribution is denoted $R_n(t)$. Theoretical work using different methods has shown that, for growth kinetics induced by gas diffusion between neighbouring bubbles driven by the Laplace pressure, $\rho(r, t)$ converges to a time independent law if it is expressed as a function of the reduced variable $r/R_1(t)$. The distributions of the topological characteristics of the bubbles also become independent of time [5]. A system of cells that shows these properties is said to be in a scaling state. In more physical

terms, one may view the foam structure at a time t_0 with a uniform magnification factor α and compare it to the structure at a later time t . If the foam is in a scaling state, there exists for each age t a factor of magnification $\alpha(t, t_0)$ such that the two structures under comparison are described by the same statistical distributions, *i.e.* $\rho(r, t) = \alpha^{-1}(t, t_0)\rho(r/\alpha(t, t_0), t_0)$. The prefactor in this expression ensures that the distribution remains normalized, whatever the time t . In general, the reference time t_0 cannot be identified with the instant of foam production. t_0 must correspond to a foam age sufficient for the sample to have reached the scaling state regime. It has been argued that assuming the above mentioned kinetics, $\alpha(t, t_0)$ must grow following the expression [6, 7]:

$$\alpha^2(t, t_0) - 1 \propto t - t_0. \quad (1)$$

In the limit of large $t - t_0$, a power law $\alpha(t, t_0) \propto (t - t_0)^{1/2}$ is obtained.

The foam structure can be probed by measuring the average fraction $T(t)$ of incident light transmitted through a sample. Due to the multiple scattering of light, its transmission may be modelled as a diffusion process. In this framework, the propagation of light is characterized by a single length scale, the transport mean free path l^* [14]. Neglecting the absorption, $T(t)$ is given by the expression [12]: $T(t) = (1 + z_e)/(L/l^* + 2z_e)$, where L is the sample thickness. z_e is the so-called extrapolation length ratio. This parameter of the order of unity depends on the reflectivity of the sample boundaries. Vera and Durian have shown that, for a foam sample inside a glass cell held in air, z_e is independent of foam age and must be taken equal to 1.24 ± 0.03 [12].

We will now discuss the influence of the coarsening process on the elastic shear modulus G' of foam. At present, *ab initio* theories of foam elasticity in three dimensions only exist for perfectly ordered samples [15–17]. We shall discuss our data using a model proposed by Princen [4] which is not based on a detailed three-dimensional structure, but on a generalization of a two-dimensional description. It predicts that the elastic properties of foam are determined by the second and third moments of the bubble radius distribution R_2 and R_3 , the surface tension σ , the liquid volume fraction ϕ and its value ϕ_c at which the real part of the dynamic shear modulus G' falls to zero. The following relation is obtained [4]:

$$G' = 1.8 \frac{R_2}{R_3} \sigma (\phi - \phi_c) \phi^\mu. \quad (2)$$

This expression has been shown to be in good agreement with the mechanical properties of concentrated polydisperse emulsions using the parameters $\mu = 1/3$ and $\phi_c = 0.71$ [4]. Recently, it has been found that emulsions with a droplet polydispersity corresponding to 10% of the mean diameter showed mechanical properties described by $\mu = 1$ and $\phi_c = 0.64$ [18]. These discrepancies show that the parameters μ and ϕ_c are not universal, but depend on the characteristics of the sample. The properties of emulsions are thought to be very similar to those of foams unless compressional stresses appear [4]. Thus, the functional form of equation (2) should apply to foams even if ϕ_c , μ and the prefactor may be inaccurate.

6. Results

Figure 1 shows the result of the step response experiment described in the experimental section. This test was performed 30 minutes and 1000 minutes after foam production. After 30 minutes, the deformation is not entirely recovered when the stress is released. Since the evolution of the compliance is the same for both gap widths, this effect is not due to wall slip. After 1000 minutes, for both gap widths, creep is no longer observed. This test shows that under a stress of 1 Pa, such coarsened shaving cream behaves as a viscoelastic solid. The slight

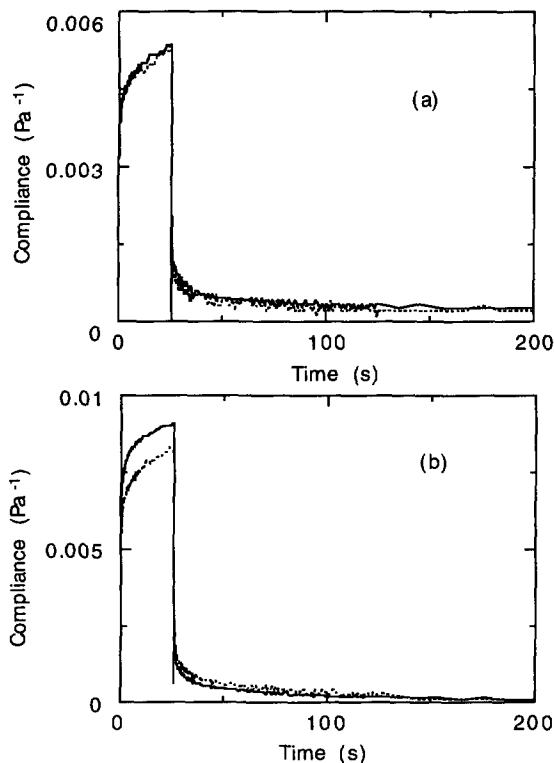


Fig. 1. — The compliance of a foam sample sheared for 25 seconds by a stress of 1 Pa is represented as a function of time, at two different foam ages (a) 30 minutes, (b) 1000 minutes after foam production. Measurements were performed with effective gap widths equal to 5.3 mm (continuous line) or to 3.3 mm (dotted line).

difference between the compliances at the two gap widths is comparable to the scatter of experimental data for a given gap and different samples. The step response experiment shows that wall slip is not observed whatever the age of the foam.

The real part of the shear modulus is represented in Figure 2 as a function of foam age. The measurements carried out at frequencies of 1.6 Hz and 0.04 Hz only differ by a constant factor. The small increase of G' with frequency reflects the viscoelastic behaviour of the sample.

Figure 3 shows the light transmission data, obtained with a vertical cell, as a function of foam age. The measured intensity is normalized by its value at an arbitrary reference time equal to 60 minutes. This ratio is equal to the fraction of transmitted light normalized in the same way, called $T(t)/T(60)$. To check for drainage effects, the measurements were carried out with horizontal as well as with vertical cell orientations. We did not observe any significant differences.

7. Discussion

Let us discuss the consequences of the scaling state hypothesis for the physical properties of foam that we have measured. We suppose that all the information about the foam structure, needed to predict these quantities, is contained in the bubble size distribution, which is

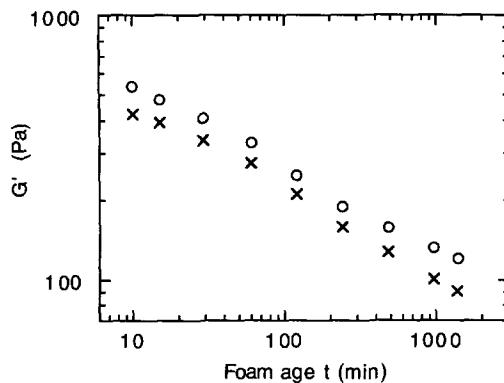


Fig. 2. — Elastic storage shear modulus of foam as a function of foam age. The sample is subjected to an oscillating shear stress of an amplitude of 1 Pa, and a frequency of either 0.04 Hz (crosses) or 1.6 Hz (circles). The effective gap width is 5.3 mm.

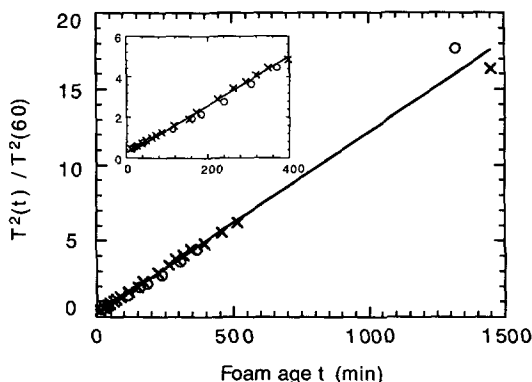


Fig. 3. — Temporal evolution of the squared normalized optical transmission defined in the text. Data for two different samples (crosses and circles) are shown. The continuous line represents a linear fit. The inset shows data at short times on an expanded time scale.

characterized by its moments. As shown in the Appendix, the scaling state hypothesis implies the following time dependence of the moments $R_n(t)$

$$\frac{R_n(t)}{R_n(t_0)} = \left(\frac{R_1(t)}{R_1(t_0)} \right)^n \quad (3)$$

where t_0 is an arbitrary reference time. Thus, the time evolution of all the moments $R_n(t)$ is governed by a single length scale which may be chosen as $R_1(t)$. Applied to expression (2), this result implies that the shear modulus G' is proportional to the inverse of R_1 . Moreover, since in the diffusion approximation, the optical transmission is governed by the single characteristic length l^* , one may conclude that $l^* \propto R_1(t)$. Indeed, the following relationship has been deduced from experiments on aqueous foam [11]:

$$l^* = (7 \pm 1)R_1. \quad (4)$$

As a consequence of formulae (2, 4) and the scaling state hypothesis, the optical transmission must show the same time evolution as the inverse of G' corrected for the small variations of the gas volume fraction. This prediction is very robust with respect to corrections to formulae (2) and (4) as shown in the Appendix.

Let us now discuss the optical transmission results shown in Figure 3. These data are in good agreement with the pioneering work of Durian *et al.* who first presented evidence for a scaling state at long times in shaving cream [8]. Since in the experiments reported here a large sample thickness was chosen, $T(t)$ can be considered to be simply proportional to l^* , the nonlinearity due to z_e being negligible. The arguments presented above show that $T(t)$ is proportional to $R_1(t)$ and therefore to $\alpha(t, t_0)$ for a given reference time t_0 . Thus, according to the scaling law (1), $T^2(t)$ represented as a function of time should give a straight line. Figure 3 shows that our data are in excellent agreement with this prediction for foam ages as short as 10 minutes after foam production. This is surprising since numerical simulations have suggested that three-dimensional foams should reach a scaling state only after a strong increase of the characteristic length [5, 6]. Aerosol generation of foams, as used for the shaving cream studied here, might lead to a structure that is already close to being statistically self-similar.

Before discussing our rheological data, let us recall previous results. Khan *et al.* have studied the dynamic shear modulus of an aqueous foam whose formulation is based on sodium alkyl sulphates, dodecanol, butyl alcohol and high molecular weight polyethylene oxide [1]. The gas volume fraction was in the range 0.92 to 0.97. They found that the modulus slightly increases with volume fraction and with shear oscillation frequency. In contrast to our experiments, all of their measurements were performed no more than 10 minutes after foam production and they did not investigate the effect of ageing. Recently, Coughlin *et al.* have measured the modulus of a Gillette shaving cream by a punch indentation test for foam ages ranging from 10 to 330 minutes [19]. No measures were taken to prevent evaporation of the liquid contained in the samples [20]. In order to avoid vertical volume fraction gradients, the foam was periodically reformed between successive measurements. Since the foam structure is perturbed by this procedure, one may wonder whether the theoretical predictions of a scaling state still apply under such conditions. Furthermore, the scatter of their data makes it difficult to deduce the time dependence of G' accurately.

In our experiments, the foam is never subjected to a stress superior to 1 Pa which is below the limit of elasticity. We therefore assume that the foam structure is not perturbed. We calculate $R_3(t)/R_2(t)$ from the measured values of G' using (2). In this analysis, the small evolution of the gas volume fraction with time is taken into account using $\mu = 1/3$ and $\phi_c = 0.71$. The uncertainty of these parameters does not have a significant influence here due to the small variations of ϕ . To eliminate the unknown prefactor in (2), the calculated ratio $R_3(t)/R_2(t)$ is normalized by its value at a reference time equal to 60 minutes, as for the optical data. In Figure 4, we show a comparison between the time evolution of the characteristic length thus obtained and the theoretical prediction that, for long times, it should evolve as the square root of foam age. For times above 100 minutes, a good agreement is observed. The deviations at short times are well-described by a parabolic law given by (1). We notice a slight deviation for the last two rheological data points. This effect may be related to an exchange of gas between the foam, initially filled with a mixture of butane and propane, and the air above the sample. Indeed, we observe such an effect at foam surfaces exposed for several hours to air saturated with moisture. Furthermore, when a shaving cream sample is placed in a cell, saturated with moisture, and whose air is saturated with ether, it rises much more rapidly than in the absence of this vapour, whereas when the cell is saturated with octane, the rise is suppressed [21]. The gas exchange rate depends strongly on the permeability of the films, determined by the solubility and the diffusion coefficient of the gas molecules in the liquid. Deep inside the sample

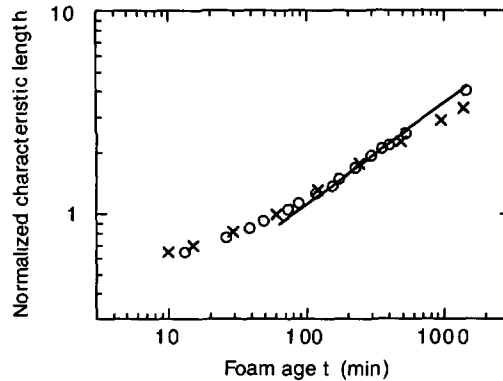


Fig. 4. — Time evolution of the characteristic lengths obtained from rheological (crosses) and optical (circles) measurements. Both quantities are normalized by their value at a foam age equal to 60 minutes. The continuous line represents a power law of exponent 0.5, fitted to the optical data at foam ages above 60 minutes.

cell of the rheometer, the effect of gas exchange begins to have an influence only after some delay, and at short times, the foam evolves as if it were placed in a sealed cell. However, about 1000 minutes after foam production, the gas exchange might modify the foam structure in the sensitive region of the rheometer.

The experimental time evolutions of the characteristic length scales obtained from light transmission data and from mechanical properties respectively are compared in Figure 4. The two data sets superpose remarkably well, in full agreement with the prediction derived from the scaling state hypothesis. However, in the absence of an accurate theory relating l^* to the foam structure, it cannot be excluded that both physical properties might depend on the same characteristic length.

8. Conclusion

We have studied the rheological and optical properties of Gillette shaving cream as a function of foam age. The temporal evolution of each property is governed by the growth of characteristic length scales which may be obtained from the moments of the bubble size distribution. The scaling state hypothesis implies that all of these quantities can be derived from the evolution of a single independent characteristic length. Our data are in full agreement with this prediction. Furthermore, the observed time evolution follows the parabolic growth law theoretically predicted for coarsening dominated by gas diffusion. We intend to investigate to what extent these laws depend on the physical and chemical properties of the foam and on the way it has been produced.

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Appendix

The moment of order n of the radius distribution, at time t , is defined as:

$$R_n(t) \equiv \int_0^{\infty} \rho(r, t) r^n dr. \quad (\text{A.1})$$

According to the scaling hypothesis, the normalized probability densities at times t_0 and t are related by the expression:

$$\rho(r, t) = \frac{\rho(r/\alpha(t, t_0), t_0)}{\alpha(t, t_0)} \quad (\text{A.2})$$

where $\alpha(t, t_0)$ is the factor of magnification discussed in the paper. Thus, $R_n(t)$ can be expressed as:

$$R_n(t) = \frac{1}{\alpha(t, t_0)} \int_0^{\infty} \rho\left(\frac{r}{\alpha(t, t_0)}, t_0\right) r^n dr. \quad (\text{A.3})$$

After a change of variable, one gets:

$$R_n(t) = \alpha^n(t, t_0) R_n(t_0). \quad (\text{A.4})$$

For $n = 1$, one obtains: $\alpha(t, t_0) = R_1(t)/R_1(t_0)$, which can be substituted in (A.4) to yield equation (3). Thus, the factor of magnification is equal to the ratio of the mean bubble radii at times t_0 and t .

As we noted in the theoretical section, the dependence of G' on the bubble size distribution, given by (2), was not derived from first principles but rather inferred from the experimental evidence. One may therefore wonder whether our conclusions would be changed if the surface-volume mean radius R_3/R_2 were replaced by some other mean bubble radius. A dimensional argument using (A.4) shows that whatever average is used to obtain the mean radius, G' will always be proportional to R_1^{-1} . A similar analysis applies to the case of the light transmission, since according to our knowledge, there is not any accurate theory relating l^* to the foam structure. Thus, the scaling state hypothesis implies that the temporal evolution of both characteristic length scales obtained from optical and mechanical data must be governed by that of R_1 under quite general assumptions.

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