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SHEAR-INDUCED NORMAL STRESS DIFFERENCES IN AQUEOUS FOAMS

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Summary We have studied experimentally the shear induced normal stress response of aqueous foams, using a new experimental approach. The data are compared to predictions derived from a general theorem of nonlinear elasticity as well as to an elasto-plastic behaviour, suggested by recent numerical simulations.

Introduction - Aqueous foams are concentrated dispersions of gas bubbles in water, stabilized by small amounts of surfactants. Even though they are constituted only of fluids, these materials show solid-like viscoelastic behaviour when they are subjected to very small stresses. If the stress is progressively increased, the structure yields and plastic flow sets in. This rheological behaviour as well as the low specific weight of foams give rise to a great variety of applications, ranging from oil production to fire fighting, the floatation of minerals, pharmaceutical products, and many forms of food [1]. Yielding typically occurs at strains of the order of 0.1-1, sufficiently large so that nonlinear elastic behaviour may be expected before the onset of significant plastic flow. For an elastic homogeneous isotropic solid, a finite shear strain γ in a direction 1, with a displacement gradient in a perpendicular direction 2, is well known to induce not only a shear stress σ_{12}, but also normal stress differences $N_1 = \sigma_{11} - \sigma_{22}$ and $N_2 = \sigma_{22} - \sigma_{33}$. Comparing measured normal stresses *as well as* shear stresses to predicted values constitutes a severe test, allowing to validate theoretical rheological constitutive laws. Concerning the first normal stress difference on which the present paper is focussed, it has been shown using very general theoretical arguments that in any elastic isotropic body with an isotropic reference state the relation $N_1 = \sigma_{12}\,\gamma$ describing the Poynting effect must hold [2]. In the elastic regime where $\sigma_{12} = G\,\gamma$ where G is the shear modulus (which may weakly depend on γ), one expects $N_1 = G\,\gamma^2$. This result is in excellent agreement with quasistatic numerical simulation of disordered dry 3D foams [3] as well as with analytical models based on a statistical description of the foams structure [4,5,6]. However, these approaches ignore the fact that real foams are by no means perfectly elastic: there is significant dissipation due to the bulk viscosity in the liquid films, the interfacial viscoelasticity of the surfactants and the intermittent local structural rearrangements induced by the Laplace pressure driven diffusion of gas between neighbouring bubbles ("coarsening process") [1]. As a consequence, it is a priori unclear to what extent the relation $N_1 = \sigma_{12}\,\gamma$ holds for real foams. Moreover, foams and yield stress fluids in general conserve a "memory" of their flow history. Pre-shearing procedures may create to some extent a well defined initial state of the system, but it is not possible to eliminate uncontrolled trapped internal stresses completely. Therefore, the existence of a well defined stress free isotropic reference state in real foams is questionable. This fundamental difficulty which we have resolved using a new experimental approach may explain the absence (to our knowledge) of any previous published experimental normal stress data for foams and many other yield stress fluids in the solid-like regime.

Methods and Materials - The foams were generated by injecting nitrogen gas containing perfluorohexane vapour and a foaming liquid into a column filled by a close packing of glass beads, as described elsewhere [7]. The liquid was an aqueous solution of α-olefin sulfonate (AOK, Witco Chemicals), Polyethylene-oxide (Aldrich) and dodecanol (Aldrich). Foam gas volume fractions of 0.92 and 0.97 were produced. For the rheological measurements, we used a Bohlin CVOR rheometer (cylindrical Couette geometry) as well as a special purpose cone plate rheometer, allowing to measure N_1 with a very high sensitivity. Measuring the response to oscillating shear is the key for a successful study of normal stresses in solid-like yield stress fluids. For an elastic sample where $N_1 = G\,\gamma^2$, with $\gamma = \gamma_o \,\mathrm{Cos}(\omega t)$, one expects a first normal stress oscillation Fourier component of frequency 2ω and amplitude (denoted $N_{1,\,2\omega}$ in the following) equal to G/2. If some uncontrolled trapped shear strain which may even slowly evolves with time is superposed to γ, this will not alter the second harmonic stress oscillations but create a superposed normal stress oscillation of frequency ω which can easily be discarded experimentally using the lock-in detection technique. Of course, this simple argument needs to be refined, since trapped strains can be of any orientation and tensorial nature. We have studied this question by rigorous calculations for sample materials described by the Mooney-Rivlin class of constitutive equations, confirming the very efficient suppression of artefacts related to trapped stresses in measurements using oscillating strains. Let us note that we have recently shown theoretically that aqueous foams may be expected to behave indeed following a Mooney-Rivlin law in the solid like regime [6]. Besides the normal stress measurements, we have also studied the shear stress response to an imposed oscillatory shear strain. For small strain amplitudes, such data can be described by the usual complex shear modulus. At large strain amplitudes, the stress response contains a spectrum of harmonics, but they remain much smaller than the fundamental stress oscillation, even up to the yield strain. We therefore discuss the results in terms of a generalized complex shear modulus, calculated from only the fundamental harmonic component of the stress oscillation. A discussion of the harmonics will be presented in future work. All rheological experiments were carried out at a frequency of 1 Hz, so that an approximately quasistatic response can be expected. To check for strain localization effects, the free edge of the sample was observed during the experiment.

Results and Discussion - Fig. 1A shows an example of the results obtained in the present study, for a gas volume fraction of 0.92. The rapid continuous drop of the real part G' of the generalized complex shear modulus and the maximum of the imaginary part G" indicate the onset of plastic flow and finally of yielding. The continuous line is the behavior theoretically expected for an ideal elastoplastic material, subjected to an imposed oscillating shear strain. The yield stress is the only free parameter of this fit of G' as well as G". The data suggest that dry aqueous foams behave at least approximately as elastoplastic materials under quasistatic conditions.

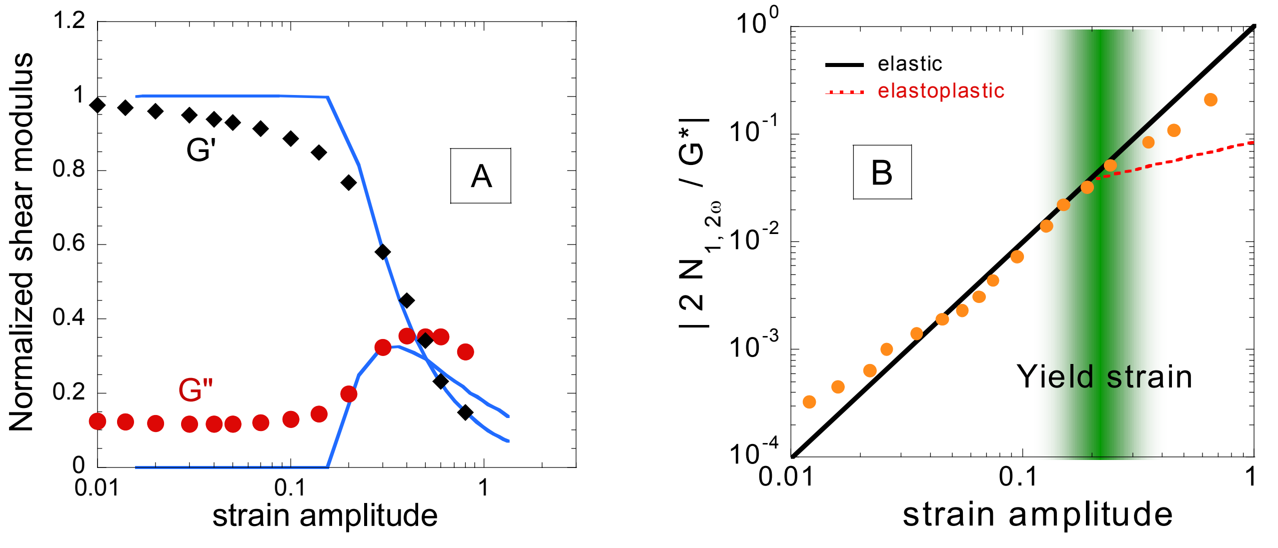

***Figure 1** Fig 1A shows the generalized complex shear modulus defined in the text, normalized by its real part obtained in the limit of small strains. The two continuous lines represent a fit to the ideal elastoplastic law described in the text, using a single free parameter. Fig 1B shows, as a function of strain amplitude, the amplitude of second harmonic normal stress oscillations, normalized by half the absolute value of the complex shear modulus. The continuous line shows the behaviour expected for an elastic body. Beyond the onset of plastic flow, represented by the thick vertical line, the dashed line corresponds to the behaviour theoretically expected for elastoplastic behaviour.*

Figure 1B shows the normalized second harmonic normal stress oscillation amplitude, in response to the same oscillating shear as in Fig 1A. The quadratic scaling with strain amplitude expected for elastic materials is clearly observed, over a decade in strain amplitude. Indeed, we have obtained theoretical arguments strongly suggesting that the influence of viscoelastic dissipation on the normal stress response is negligible in foams at low frequencies, as long as G' >> G". Close to the yield strain, plastic flow is expected to play an important role. In this regime, the signature of elastoplastic behaviour would be a cross-over to a scaling with an exponent ½, smaller than the one found experimentally. Our next objective is to develop a more physical constitutive model, taking also into account the dissipation effects mentioned in the introduction. A key feature of a more quantitative model may be the mesoscopic fluctuation of mechanical properties in foams, as described by the recent SGR class of models [8, 9].

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