RHEOLOGY OF FOAM NEAR THE ORDER-DISORDER PHASE TRANSITION.

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INTRODUCTION

Foams are extremely important in a variety of industrial applications. They are widely used in firefighting applications, including the Fire Suppression Systems aboard the Space Shuttle and Spacelab module. The petroleum industry utilizes foams in flow applications such as enhanced oil recovery and as drilling fluids. They are used in various industries as trapping, transport and separation agents. Arguably the most important quality of a foam in many of these industrial processes is its response to imposed strain, or its rheological behavior. Yet there exists almost no experimental data on the rheological properties of real 3D foams. This is due in large part to the earth-based requirements for contact containment, and to the fact that gravity-induced drainage quickly destroys all but the "driest" foams, those with a very high gas volume fraction \( \phi \). We will develop a unique method to provide non-contact control and manipulation of foam samples. The development of this technique, together with experimentation in 0g, will provide the ability to carry out a set of benchmark experiments which will allow determination of a foam's yield stress, bulk modulus and viscosity as a continuous function of gas volume fraction from the dry limit \( \phi \approx 1 \) through the order-disorder phase transition to the wet limit \( \phi \approx 0 \) of a bubbly liquid. In addition to providing the first measurements of such quantities as functions of \( \phi \) to compare with theory, the knowledge gained will have practical application to the myriad actual uses of foams on the earth, and to space-based systems.

PROBLEM STATEMENT

Figure 1. A side (left) and top (right) view of a foam drop approximately 0.75 cm in diameter. The drop is levitated in a 23 kHz acoustic standing wave field. Note that, while the drop is almost spherical from the top view, the high acoustic pressure required to levitate in 1g has caused significant deformation shown in the side view. Gravity acts in the vertical direction in the side view. This is a dry, fine foam.

Before we define the problem, we present the target of our investigation: a "foam drop". By this we mean a sample of foam which is not in contact with any solid boundaries. Figure 1 presents a video image of an example foam drop which is levitated in 1g in the laboratory.

The scientific objectives of the research are:

1) To develop a novel acoustic technique for measuring static and dynamic stress-response properties of foams. Foam drops (where the number of individual bubbles is very large) will be levitated in 1g in an acoustic field, and then manipulated via the acoustic and hydrostatic forces acting on the drop. In this way, both extensional shear strain and pure dilatational strain can be applied in a controlled fashion. Both stress/strain behavior (elastic modulus, yield stress) and effective bulk shear viscosity for foams as a function of gas volume fraction, foam coarseness, and material composition will be measured. The 1g limit of volume fraction for useful experimentation will be determined, and microgravity experiments will be designed to enable these measurements to be made down to and through the order-disorder phase transition (where a foam loses its rigidity) in volume fraction.

2) To model the response of foam drops to static and time-varying modulation of the acoustic field and the ambient pressure. The purpose of the modeling will be to relate three fundamentally important rheological properties, the yield stress, the bulk elastic modulus, and the effective bulk shear viscosity, to physical observables under the two strain conditions encountered in experiments. We will treat the foam as a lumped-element continuum with a known imposed average velocity field. The quasi-static response will allow direct determination of the yield stress. By developing expressions for frequency and damping of modal oscillations of foam drops, we can infer bulk modulus and viscosity. A variety of algorithms, such as the matrix pencil method [Sarkar and Pereira, 1995] and the total least squares Prony method [Golub and Van Loan, 1980] will be assessed to extract lumped parameters from the transient data.

3) To define experiments which can be performed in the extended 2g environment, where the effects of drainage and high acoustic fields can be avoided. The ultimate goal of this project is to determine physical properties as functions of the volume fraction. Theory predicts (at least for 2D) that several phenomena become apparent only near the order-disorder phase transition, where the individual bubbles in the foam can be considered to become weakly interacting. The technique developed in objective 1 above, coupled with the lack of 1g drainage, could provide definitive measurements of elasticity and viscosity as functions of the volume fraction for 3D foams, and...
confirm some predictions of 2D theoretical work, while providing motivation for 3D theoretical work.

BACKGROUND

A foam is a very complex entity to study. At the outset, the would-be researcher is presented with the problem of multiple spatial scales. It is a two-phase composition, and the liquid phase is also a multicomponent material, which immediately suggests that any study of dynamical response properties will have to take into account multiple time scales. Such a problem might at first suggest that a detailed microscopic analysis would be in order. And yet, a foam's practical and physical importance depends on its macroscopic properties. Engineers would like to know how a foam responds to an applied strain. What are the regimes of elastic vs plastic response, and how do they vary with compositional parameters? Physicists would like to know the scaling properties in the asymptotic limits of large cell number and large times. Is the evolution of such a non-equilibrium system robust with respect to perturbations in either compositional parameters or external forces? Answering these questions entails measurements of a foam's gross properties, both topological (cell size distribution, average area, etc.) and physicochemical (bulk shear viscosity, bulk modulus, and so on). It is this crucial gap in current rheological knowledge which we seek to fill.

Foams on earth are notoriously difficult to work with. In fact, two fundamental processes, diffusion-driven coarsening ("aging") and gravity-driven drainage, ensure that a sufficient time (on the order of minutes) after the creation of a typical fresh foam, one is no longer dealing with the same substance either topologically or rheologically. Apart from some measurements of 2D rheology which are complicated by the effects of method-dependent wall-slip, the 3D rheology of foams remains largely unknown.

However, as Kraynik (1988) understatedly points out, despite the gaps in our understanding of foams, their practical uses in industrial processes "...have not been completely inhibited by unresolved fundamental issues." Foams are of tremendous economical importance in industry. Foams are widely used in firefighting applications, and are especially effective in fighting flammable liquid fires. In fact the Fire Suppression System aboard the Space Shuttle utilizes cylinders of Halon foam, which, when fired, force a rapidly expanding foam into the convoluted spaces behind instrument panels. Foams are critical in the process of enhanced oil recovery (Edwards et al. 1991; Stebe and Maldarelli, 1994), due to their surface-active and highly viscous nature. They are also used as drilling fluids in underpressurized geologic formations. They are used as transport agents, and as trapping agents. They are also used as separation agents, where ore refinement is accomplished by froth flotation of the typically lighter and hydrophobic contaminants. See Aubert et al. (1986) for a review of some popular applications.

Foams also serve as model disordered systems far from equilibrium (Berge et al., 1990; Bak, et al. 1987; Stine, et al. 1990; Weaire and Rivier, 1984). The statistics of such systems, where thermodynamic equilibrium arguments do not apply, is thought to be governed by a "self-organized criticality", which can often be characterized by some multifractal scaling analysis. Whether or not this is the case for foams seems to depend upon both the volume fraction, the material, and the strain history (Weaire and Kermode, 1984). The macroscopic rheological properties which are of interest in this study will, in general, depend on the structure: a fractal foam will possess a different elastic modulus from one possessing a unimodal size distribution (Herdle and Aref, 1992).

BASICS

We must briefly introduce some basics (a comprehensive review of fundamental ideas can be found in the textbook by Edwards, et al., 1991; and, see Kraynik, 1988 for a technical overview). The fundamental unit of a foam is a gas pocket contained by a thin liquid shell. The close proximity of many such gas "cells" or "bubbles" connected by their liquid shells constitutes an elementary foam. The thin interbubble films meet at fluid vertices known as Plateau borders. The capillary pressure in the borders is balanced by the so-called disjoining pressure in the thin film region. The liquid shell is quasi-stabilized against rapid dissolution and coalescence of the bubbles by the presence of one or more surfactant species, which hinder gas diffusion and thinning flows at the interbubble boundaries. Thus the surface rheology peculiar to surfactants (especially soluble ones) will be intimately involved in both the static and dynamic mechanical properties of the macroscopic foam.

The fundamental descriptive parameter of a macroscopic foam is the gas volume fraction $\phi$. A "dry" foam is approached in the limit as $\phi \to 0$. A "wet" foam, thus, is the descriptor of decreasing volume fraction. A critical transition occurs as $\phi$ is decreased to the order-disorder phase transition (or rigidity-loss transition). As the term implies, the foam will cease to be rigid and ordered structurally, and will flow freely, becoming a bubbly liquid, as $\phi$ approaches and passes this value. This critical value, $\phi_c$, which will differ slightly for different compositions (and should also be a strain-rate dependent quantity), is related (although as yet only informally) to the value for crystal/random close-packing of hard sphere models ($\phi_c = 0.74$ or 0.63, respectively, for 2D and 3D). Just as the order-disorder transition for hard-sphere models engenders changes (and sometimes discontinuities) in the mechanical and thermodynamical properties of the
matter, so the rigidity-loss transition is the boundary of qualitative and quantitative changes in macroscopic foam properties.

The most obvious of these physical and rheological properties is the yield stress, \( \tau_0 \), which classically represents the transition from elastic to plastic response to applied strain in solids. The yield stress for a foam does not even exist until the volume fraction exceeds \( \phi_c \), and is an increasing function of \( \phi \) thereafter. Likewise, the shear elastic modulus \( G \), does not exist for a fluid, and only starts to exist and increase as \( \phi \) is increased beyond \( \phi_c \). The dilatational elastic modulus \( G_d \) will depend on both the topology of the foam and the surface elasticity (both intrinsic and Gibb's (see Edwards et al., 1991)), which will be material dependent. The bulk shear viscosity at gas volume fractions below \( \phi_c \) is dominated by the bulk shear viscosity of the host liquid, with only minor perturbations due to the presence of surfactants and bubbles in the bulk. But the effective bulk shear viscosity, \( \mu_e \), of a foam beyond \( \phi_c \) is dominated by the effects of surfactant-induced surface viscosities, and topological structure and processes. The effective foam dilatational viscosity \( \kappa \), which will be a measure of purely dilatational flow dissipation, will be an important quantity with which to quantify the effects of different surfactant materials, since in pure dilatational motion, no topological processes will occur.

**INVESTIGATIVE APPROACH**

**Experimental Methods**

For 1g and mg (parabolic aircraft flights) experiments, we will use acoustic levitation techniques for positioning and induction of extensional shear strain (the techniques will have to be modified somewhat for mg, since only small positioning forces will be required). The basic method is one which has been developed by Trinh and coworkers (Trinh, 1986; Trinh and Hsu, 1986a and 1986b) and extended by Tian et al., 1995 and Holt et al. 1997. Pure dilatational strain will be applied to a levitated sample by varying (as a step function and periodically) the ambient (hydrostatic) pressure. Sample deformation will be measured via an optical extinction technique and via video techniques (Trinh, Holt and Thiesen, 1996). This section will highlight features of the apparatus and method. We will also discuss diagnostic measurements necessary to characterize our foam samples.

Figure 2 presents the salient features of an acoustic levitation apparatus. This technique has been successfully used to perform liquid drop experiments in air (Marston and Apfel, 1979; Tian et al., 1993). A single foam 'drop' will be levitated in air. The foam drop is acoustically levitated in a doubly resonant standing wave pressure field in the air gap between the horn and the reflector. The acoustic pressure is varied sinusoidally at approximately 20 kHz. Nonlinear radiation pressure serves to hold the foam in a fixed position slightly above a pressure node, where the buoyant force is balanced (Doinikov, 1994). In practice, this limits the upper range of foam drop radii to 1 cm at an operating frequency around 20 kHz, and correspondingly larger at lower frequencies.

Figure 2. Schematic of a foam drop levitator enclosed in a pressure vessel.

The foam drops we will levitate will be comparable in size to the acoustic wavelength. If \( k \) is the acoustic wavenumber in air, and \( R_0 \) is the foam drop radius, then the size parameter \( kR_0 \) will be of order 10\(^4\). For these values of \( kR_0 \), the time-average acoustic radiation pressure (which is responsible for balancing the gravitational force) is distributed non-uniformly over the bubble surface (Marston (1980); Marston et al. (1981); Tian et al. (1993)). By varying the acoustic pressure amplitude \( P_e \), we can vary the magnitude of the imposed strain, which is axisymmetric and approximately extensional shear (Weaire and Kermode, 1984). The amplitude can be varied as a step function, quasi-statically, or be periodically modulated, without affecting stable levitation of the drop. The frequency of the modulation will be swept to find the fundamental resonance of the quadrupole eigenmode (with respect to the velocity field, where there exist 4 velocity nodes) This fundamental, lowest energy shape oscillation mode can be described spatially by the order 2 axisymmetric spherical harmonic function \( Y_{20} = Y_{20} (\theta, \phi) \) with a time-varying amplitude coefficient. Figure 3 shows a levitated foam drop in 1g undergoing quadrupole modal oscillations. The foam was created by bubbling air into a solution of water and Kodak Photoflo. The resonance frequency of the quadrupole mode was approximately 150 Hz.

The imposition of pure dilatational strain will be accomplished by varying the ambient pressure of a containment chamber surrounding the acoustic levitation apparatus. This can be effected because the foam will possess a capillary overpressure \( P_e = 2\sigma/S/\nu \) due to surface tension. By varying the ambient pressure \( P_e \)
the equilibrium ratio $S/V$ will change, and the foam drop will either expand or contract in response. $P_0$ can be varied as a step function, quasi-statically, or be periodically modulated, although this will affect the levitation conditions somewhat.

**Figure 3.** A coarse foam drop levitated in an apparatus similar to Fig. 2. On the top, the drop is levitated but not modulated. The modulation frequency was swept until a resonant maximum in the response was observed at approximately 150 Hz for this drop. The drop on the bottom depicts the time-averaged (the shutter speed was 1/60 sec) quadrupole ($n = 2$) oscillations of the drop.

Our primary observables for the experiments will be the drop shape (and its deformation) and volume as a function of time. These will yield relaxation, frequency and damping quantities, depending on the temporal nature of the applied strain. Regardless of the type of strain imposed, deformation information can be obtained in two complementary ways. Time and space resolved video images will yield the full surface outline of the drop. Thus, absolute spatial deformation can be measured, and temporally resolved up to a Nyquist frequency of 15 Hz. Digital image processing techniques will be used (Trinh et al., 1994) to automatically acquire and obtain geometrical measurements on sequences of images, typically with 100 micron resolution. For the oscillatory measurements, an optical extinction method (Tian et al., 1995) can be used to obtain frequency and amplitude information which requires much less digital storage space and post-processing. The Nyquist frequency will be upwards of 100 kHz for this type of data collection, which will be easily enough dynamic range.

**Diagnostics**

Several characterization measurements must be made in order to tie rheological behavior to both topological and material parameters. These are not as straightforward as one might hope, and so we must explore, modify and customize existing techniques, as well as perhaps invent new ones. In this sub-section, therefore, we will present viable candidates for such measurements, but note at the outset that these may not be the only ones we will ultimately use.

The most important topological parameter which must be reliably measured and controlled is the volume fraction $\phi$. A direct measurement in a 3D configuration is only possible in the small component limit, where a video tomography measurement could be used (Thomas et al., 1995). A direct measurement in a 2D configuration is possible. The foam sample could be confined between two transparent plates, and the 2D image could thus be analyzed directly (Glazier et al., 1987; Khan et al., 1988). Capillary wetting could be minimized in order to avoid an underestimate of the liquid present.

Several indirect methods also suggest themselves. $\phi$ is related to the surface/volume ratio $S/V$, which is related to the capillary pressure via the surface tension. Thus, a measurement of the capillary pressure via either the monopole (dilatational) oscillation mode frequency, or directly by monitoring decomposition in a closed cell (Stamenovic and Wilson, 1984).

The distribution of cell radii or area $P(a)$ is also important: from such a measurement, the order parameter $m_2$ could also be determined. $P(a)$ could be measured directly using the above mentioned methods of tomography or spreading between plates. The temporal variation of $P(a)$, and hence also of $<a>$ (and thus the scaling, if it is present) could be determined using an optical scattering technique developed by Durian et al. (1991).

The fluid material composition and surface rheology must also be determined. Compositional concentration of surfactants will be controlled in production, but relevant surface rheological parameters must be measured. The time-dependent surface tension can be measured via digital pendant-drop tensiometry (Lin, Mckeigue and Maldarelli, 1990), which we currently employ as a fluid diagnostic in our lab. Surface (Gibbs') elasticity and viscosity can be inferred via a liquid drop oscillational method (Tian et al. 1995)
which can utilize the same levitation apparatus as the foams.

Our current plans call for the host fluid to be water. Candidates for surfactant materials which have well-studied surface properties include non-ionic polyethoxy types (Triton-X-100, for example, Brij series, Tween series), proteins (BSA), and certain ionic types (SDS, anionic; DTAB, CTAB, cationic). Alcohols such as decanol and pentanol are often used, although an alcohol in water alone will not produce a stable foam. In order to compare to some previous measurements, some complicated formulae will also be used: glycerin/water and sodium oleate (Sun et al., 1994); decanol, butyl alcohol, water, polyethylene oxide, and Witconate AOK (Khan et al., 1988). It will be important to establish a connection to these earlier results.

**Procedure**

**Foam production**

There exist many ways to obtain foams of varying size distribution, material composition, and volume fraction. Bubbling (whether active or passive) a gas through the liquid phase is a way to obtain a relatively coarse foam. Forcing flow through a cellular lattice or packed column is a popular method to obtain fairly fine foams. Air-aspirated generation, where the liquid phase is sprayed onto a more or less fine mechanical grid, is a good technique for producing very dry foams. Forced pipe flow in small diameter tubes (Khan et al., 1988) is a good way to vary the volume fraction by varying the tube diameter. Ultrasonic agitation of the liquid phase is a final way to obtain a fairly polydisperse size distribution foam. For our purposes, many of these methods will be employed in order to obtain the characteristics we need. Once obtained, the foam sample must be shaped in a nearly spherical form. The sample must then be successfully transferred to the trapping region of the acoustic field.

**Variation of parameters**

The levitating pressure will be varied between approximately 150 dB and 170 dB. Suppressed carrier modulation will be used to periodically modulate the levitation field, thus minimizing the oscillation (present in simple AM) of levitation position. Modulation frequencies will range from 1 to 500 Hz. After initial location of modal frequencies, computer-controlled pressure-frequency schedules will be initiated to obtain response curves as the frequency is swept. The ambient or hydrostatic pressure will be varied from 0.5 atm to 1.5 atm (the lower limit is determined by levitation stability in the reduced pressure).

For each of the above experiments, the effect of varying the concentration of one surfactant component will be investigated. Since these will be well-characterized surfactants, we will be able to infer the dependences of the foam rheological properties on the surface rheological properties which will change as the concentration changes.

Finally, for all of these experiments, the volume fraction will be varied from the dry limit (\(\phi = 1\)) down to the minimum attainable in \(\text{lg}\) (about 0.9 for our measurements). The increments will be fine enough to enable preliminary assessment of the functional dependence of rheological properties on \(\phi\).

The deformation data obtained will be analyzed digitally, as will the optical extinction data. The yield stress will be measured directly from the relaxation after a quasistatic strain variation. Elastic moduli will be obtained from step-function pressure (acoustic and ambient) variation. Elastic moduli and viscosities will be obtained from periodic pressure oscillations.

**MICROGRAVITY RATIONALE**

All but the driest foams drain in gravity. The liquid component will flow downward, and the bubbles will rise until a pool of liquid with a dry foam cap will form. Gravity will thus prevent the measurement of any properties as the gas volume fraction is decreased towards the order-disorder transition, because the foam will be destroyed. Even a dry foam has a finite weight. Thus, it must be supported against gravity, but preferably without container contact, whose forces can dominate. Thus, experimentation is frustrated by gravity. Acoustics in \(\text{lg}\) can alleviate the contact problem, but at the expense of requiring intense acoustic fields causing undesirable nonlinear acoustic effects. The first of these is the resulting static deformation even at minimum trapping pressure -- a spherical equilibrium drop cannot be obtained, nor can the limit of zero strain be achieved. Secondly, at such high pressures, acoustic streaming flow occurs, which can cause uncontrolled sample rotation. This will not only hamper attempts to obtain known strain, but will have the undesirable effect of drying out the foam prematurely.

The most important control parameter for rheological experiments is the volume fraction \(\phi\). Yet the useful range for \(\text{lg}\) experimentation is \(\phi > 0.92\), which is well above the rigidity loss transition. The unavoidable fluid drainage destroys the essentially isotropic nature of a foam for wet foams. Imposition of slow rotation about a horizontal axis (a clinostat, see Cengel and Lemlich, 1989) can minimize drainage effects, but has only proven effective for \(\phi > 0.89\), which is again well above \(\phi_c\). Thus, in \(\text{lg}\) we are limited to experimentation with very dry foams.

Certainly \(\text{lg}\) measurements are important in their own right, and indeed have already proven feasible, as shown in Fig. 2. As Kraynik has pointed out, experimental measurements, especially systematic measurements such as we envision, are sorely lacking in the literature. Thus the reporting of parameter dependences for foam rheological properties will be a valuable contribution to the knowledge of foams. In addition to their intrinsic importance, \(\text{lg}\) measurements will set limits for parameters to be investigated in \(\mu\text{g},\)
and provide bounding values for the foam rheological properties under study.

But the 1g measurements can only probe the dry foam limit. Thus, measurements of important physical phenomena near the critical volume fraction cannot be performed in 1g. The experiments require more than just a few seconds of low gravity. The time scales involved for a single frequency sweep are on the order of several minutes, and that would be just one data point! Performing rheology experiments on aging foams to study the effects of the scaling/non-scaling behavior would require times on the order of an hour or so. Thus, extended low gravity, such as aboard the Spacelab module or aboard the space station, is absolutely necessary to carry out the full range of experiments.

Thus, for all these reasons, it is desirable to perform foam rheology experiments in microgravity. The dominance of surface tension forces and the lack of a buoyant/weight force would a) guarantee an external-stress-free equilibrium condition; b) eliminate fluid drainage from the interbubble regions; and c) eliminate nonlinear effects of intense acoustic fields. A smooth variation of the volume fraction from 1.0 down through 0.63 and into the bubbly liquid limit would enable the determination of quantities which are continuous (viscosity) and discontinuous (modulus, yield stress) at _c_.

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