Coupled elasticity in soft solid foams
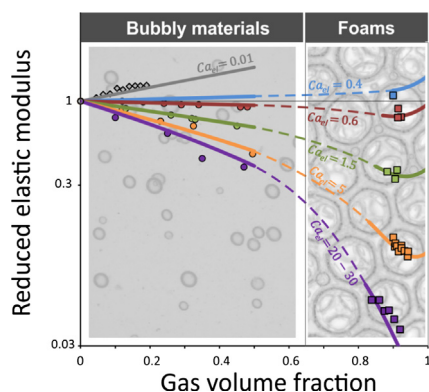
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GRAPHICAL ABSTRACT

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Elasticity of soft materials can be greatly influenced by the presence of air bubbles. Such a capillary effect is expected for a wide range of materials, from polymer gels to concentrated emulsions and colloidal suspensions. Whereas experimental results and theory exist for describing the elasto-capillary behavior of bubbly materials (i.e. with moderate gas volume fractions), foamy systems still require a dedicated study in order to increase our understanding of elasticity in aerated materials over the full range of gas volume fractions. Here we elaborate well-controlled foams with concentrated emulsion and we measure their shear elastic modulus as a function of gas fraction, bubble size and elastic modulus of the emulsion. Such complex foams possess the elastic features of both the bubble assembly and the interstitial matrix. Moreover, their elastic modulus is shown to be governed by two parameters, namely the gas volume fraction and the elasto-capillary number, defined as the ratio of the emulsion modulus with the bubble capillary pressure. We connect our results for foams with existing data for bubbly systems and we provide a general view for the effect of gas bubbles in soft elastic media. Finally, we suggest that our results could be useful for estimating the shear modulus of aqueous foams and emulsions with multimodal size distributions.

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1. Introduction

Aerated materials are widely encountered as products from various industries. Polymer foams, such as polystyrene or polyurethane foams are emblematic examples showing unique properties that have been proved to be useful for numerous applications.

Nomenclature

γ	liquid/gas surface tension
R	bubble radius
E_0, G_0, G_0'	elastic modulus of the interstitial material (emulsion)
$Ca_{e\ell} = RG_0'/\gamma$	elasto-capillary number
ϕ	gas volume fraction in emulsion foam
ϕ_0	gas volume fraction in the precursor foam
ϕ_c	packing volume fraction of bubbles
φ_{oil}^0	oil volume fraction in mother concentrated emulsion

φ_{oil}	oil volume fraction in interstitial phase of emulsion foam
φ_{oil}^c	packing volume fraction of oil droplets in oil/water emulsion
$G'(\phi, G_0')$ or $G'(\phi)$	shear elastic modulus of emulsion foam at gas volume fraction ϕ (and interstitial elastic modulus G_0')
$G'(\phi, 0)$	shear elastic modulus of aqueous foam at gas volume fraction ϕ

Aerated cement concrete is another example where lightness and mechanical strength have to be optimized in order to provide suitable construction materials [1]. The mechanical properties of such systems have been widely investigated in relation with the microstructure arising from the organization of bubbles and solid matrix in the material [2]. Depending on incorporated air volume fraction, the mechanical strength is estimated from the effect of holes (voids) in the bulk matrix [3,4] or from the mechanical behavior of microstructural elements forming the solid skeleton of the material [2]. It is worth noting that the effect of capillarity is not accounted for because the elastic modulus E_0 of the matrix, typically from 1 MPa to 10 GPa, is large compared to the surface energy effects.

It is however possible to deal with more soft elastic matrices, characterized by elastic modulus much closer to capillary pressure. This is the case for some extremely soft polymeric gels, such as polydimethylsiloxane (PDMS) and polyacrylamide (PAA) [5], as well as for several biopolymers [6,7], such as cross-linked networks of actin or fibrin, and gelatin. This is also the case for most of the so-called soft glassy materials [8], such as concentrated emulsions, dense granular suspensions and pastes. In terms of rheology, those materials exhibit a yield stress, i.e. they behave like a (visco)elastic solid until a certain critical stress is exceeded. Aerated yield stress fluids are encountered in numerous application fields, such as foods, paints, cosmetics, and construction materials. For several of those materials, capillary effects has been evidenced. Style et al. [9] showed how capillary inclusions (here small liquid drops) can either stiffen or soften a polymer matrix. Ducloué et al. [10] demonstrated that the shear elastic modulus of concentrated emulsions can be tuned by incorporating well-chosen air bubbles. Such studies were mostly focused on 'bubbly' systems, for which the volume fraction ϕ of capillary inclusions is smaller than $\phi_c \approx 0.64$, the packing volume fraction of spherical inclusions. However, systems characterized by $\phi > \phi_c$, are also widely encountered. For example, biomedical foams are used for tissue engineering applications [11], and food industry develops more and more foamed products, from alginate and gelatin foams to whipped creams [12]. Foamed cement [1], geopolymer [13] or plaster [14] fresh pastes are also examples for foamy soft materials. How matrix elasticity couples with bubble elasticity in such materials? Whereas foams have been studied mainly in situations where either the solid skeleton or the bubble elasticity was governing solely their mechanical behavior, i.e., $E_0 \gg 2\gamma/R$ or $E_0 = 0$ respectively (where $2\gamma/R$ is the bubble capillary pressure), there is no available experimental or theoretical result for predicting this behavior as both contributions count, i.e., for $E_0 \approx 2\gamma/R$. The latter is precisely the situation we investigate in this paper. We elaborate well-controlled foams made with concentrated emulsion and we measure their shear elastic modulus as a function of gas volume fraction, bubble size and elastic modulus of the interstitial emulsion. We show that emulsion foams possess the elastic features of both the matrix and the bubble assembly, and that the elastic

modulus is governed by two parameters: the gas volume fraction and the elasto-capillary number.

2. Materials and methods

Emulsion foams are prepared by mixing aqueous foam and emulsion following the procedure sketched in Fig. 1. The first step of the preparation is the production of precursor aqueous foam with well-controlled bubble size and gas volume fraction (see Fig. 1a). Foaming liquid (distilled water 70% w/w, glycerol 30% w/w, and tetradecyltrimethylamonium bromide at a concentration 5 g·L^{-1}) and perfluorohexane-saturated nitrogen are pushed through a T-junction allowing controlling the bubble size by adjusting the flow rate of each fluid. Several bubble sizes were obtained: $R = 150, 270, 300$ and $400\,\mu m$, with polydispersity $\Delta R/R \approx \pm 5\%$. Produced bubbles are collected in a glass column and gas fraction is set to an approximately constant value ϕ_0 over the foam column by imbibition from the top with foaming solution (see Fig. A1). As shown in the following, ϕ_0 has to be known as accurately as possible. From careful work on the reproducibility of foaming and drainage conditions in the column, we were able to define a target value within a range $\phi_0 \pm \phi_0$ with $\phi_0 = 0.001$ and ϕ_0 set to a value ranging from 0.985 to 0.995 (see Appendix A).

Secondarily, we use a concentrated oil-in-water mother emulsion which has been produced in advance using a Couette emulsifier. The oil is a silicon oil (V350, Chimie Plus) and the water solution is composed of distilled water 50% w/w, glycerol 50% w/w, and tetradecyltrimethylamonium bromide at a concentration 30 g·L^{-1}). Note that continuous phases of the foam and the emulsion are almost the same. The oil volume fraction is $\varphi_{oil}^0 = 0.85$ and the radius of the oil droplets measured by laser granulometry is around 1–2 μm (the polydispersity is around 20%). Note also that the oil/water/surfactant system chosen for this study is known to produce very stable mixtures of foam and emulsion [10,15–17].

In the next step, precursor foam and emulsion are mixed in a continuous process thanks to a mixing device based on flow-focusing method (see Fig. 1b). The mixing device allows tuning the flow rates of both the foam (q_{pf}^*) and the emulsion (q_0), as well as introducing additional foaming solution at a flow rate q_s in order to dilute the mother emulsion. Note that the efficiency of the dilution process has been checked separately by measuring the elastic modulus G_0' of resulting diluted emulsions as a function of oil volume fraction. In fact we prepared three mother emulsions, and for each one the curve $G_0'(\varphi_{oil})$ was determined. Typical example is plotted in Fig. 2a, showing that $G_0'(\varphi_{oil})$ curves can be described by the relationship $G_0' = g\varphi_{oil}(\varphi_{oil} - \varphi_{oil}^c)$, where g and φ_{oil}^c are close to 5100 Pa and 0.63 respectively, which is fully consistent with previous results [18]. The device produces emulsion foams with target values for gas volume fraction ϕ^* and oil volume fraction φ_{oil}^*. Note also that bubble size is conserved during the mixing step. According to parameters defined above, target values are