



Rheology of foams and highly concentrated emulsions



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ABSTRACT

We review the state of the art in foam and highly concentrated emulsion rheology, with an emphasis on progress made over the last five years. Since the structures and physico-chemical processes relevant for foams and emulsions are closely analogous, comparing the knowledge recently gained in these two neighboring fields brings fresh insight. In this spirit, we review how the macroscopic mechanical response arises from a coupling between interfacial energy and long range molecular interactions, entropic effects, interfacial rheology, and dynamics at the droplet or bubble scale. We present experiments and models concerning elasticity, osmotic pressure, yielding and flow behavior.

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1. Introduction

Foams and emulsions are soft materials that have many applications in our everyday life and in industrial processes [1,2]. Foams are gas bubble dispersions in a surfactant solution, with a packing fraction above a critical value close to 2/3 where jamming occurs. Similarly, emulsions are constituted of two immiscible liquids, for instance oil and water. Droplets containing one of the liquids are dispersed in the other one. In emulsions so concentrated that the packing fraction is above the jamming point, the droplets are highly compressed, giving rise to structures very much alike those of foams. Foams and emulsions are both stabilized by surfactant molecules that are adsorbed at the interfaces. They have similar aging mechanisms, although emulsions can be stable for months whereas foams age on much shorter timescales. They also both exhibit a similar rich rheological behavior and despite being solely constituted of fluids, their mechanical response can be either solid-like or liquid-like, depending on the applied load [1,2]. Liquid foams and emulsions share many features with other concentrated dispersions of soft particles such as microgel beads, multi-lamellar vesicles, or star polymers: structural disorder, metastability and soft elastic repulsion between neighboring particles. By analogy with molecular glassy systems, they are called soft glassy materials. Since the physico-chemical processes that govern the rheology of foams and emulsions are closely related, combining and comparing the knowledge

recently gained in these two fields can bring fresh insight. This is one of the principal aims of the present review. To simplify the text, bubbles and droplets will be referred to as “particles” and highly concentrated emulsions will be called emulsions in the following.

In this review, we highlight progress achieved over the last five years, in selected topics of current interest, concerning the rheology of foams and emulsions. We present recent experiments, numerical simulations and theoretical models about the static elasticity and the osmotic pressure (cf. Section 2), the yielding transition (cf. Section 3) and the flow behavior (cf. Section 4), where we focus on shear-banding, steady flow constitutive laws and wall slip.

2. Structure, static elasticity and osmotic pressure

2.1. Structure

The structure and dynamics of foams and emulsions strongly depend on the particle size and on the dispersed phase volume fraction ϕ [1]. Stable emulsion droplets can have a radius R below the colloidal limit ($R \lesssim 1 \mu\text{m}$) so that their thermal motion is significant while bubbles of such a size are highly unstable. In a quiescent foam or emulsion, the particles are jammed in a solid-like dense packing (cf. Fig. 1). Its free energy density reflects particle interactions due to capillary, van der Waals, electrostatic (for charged surfactants), steric or depletion forces. In equilibrium, this energy is minimal for fixed particle volumes. The interplay of these interactions sets the thickness h of the films separating neighboring particles.

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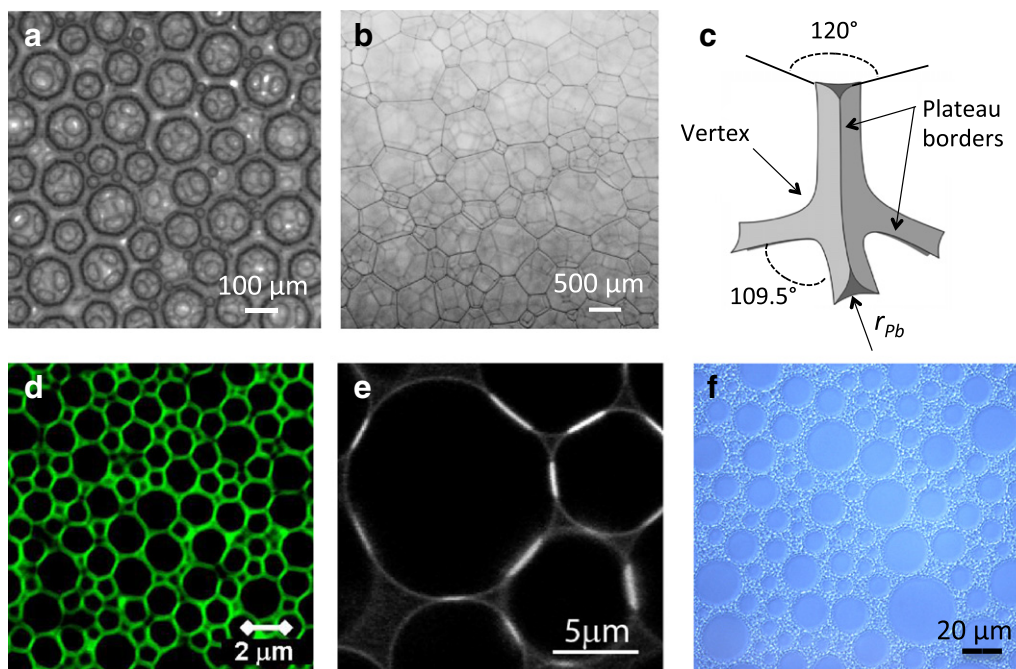


Fig. 1. Aqueous foams with gas volume fraction: a) $\phi \approx 0.64$, b) $\phi \approx 0.99$. c) Schematic structure of four Plateau borders joining at a vertex. d) Repulsive oil-in-water emulsion with oil volume fraction $\phi \approx 0.80$. Courtesy C. Locatelli-Champagne and M. Cloitre, ESPCI ParisTech. e) Adhesive oil-in-water emulsion. Regions with marked fluorescence reveal adhesive patches between neighboring droplets. Adapted from [6]. Courtesy LL. Pontani. f) Bidisperse water-in-oil emulsion with $\phi = 0.85$ made of a 80/20 volume fraction mixture of droplets of sizes 17 μm and 3 μm . Small bubbles fill the spaces between large bubbles, leading to a critical volume fraction ϕ_c much larger than that of a random close packing of monodisperse spheres. Adapted from [3]. Courtesy R. Foudazi.

In the absence of attractive interactions and if $h \ll R$, the packing structure is governed by interfacial tension [1]. As illustrated in Fig. 1b, in a “dry” foam (ϕ close to 1), the bubbles are polyhedral and the equilibrium packing obeys Plateau’s rules [1]: i) Films join 3 by 3, at angles of 120° and form slender liquid channels called Plateau borders; ii) These borders join 4 by 4 at angles of 109.5° and form tetrahedral vertices (Fig. 1c). If the packing fraction is decreased towards a critical value ϕ_c close to $2/3$, the particles become more and more spherical (Fig. 1a and d). Such foams are called “wet foams”. For $\phi < \phi_c$, they lose their contacts, the packing unjams and the dispersion no longer behaves like an elastic solid. For monodisperse particles, $\phi_c = 0.74$ for ordered face centered cubic (fcc) or hexagonally close packed (hcp) packings and $\phi_c = 0.64$ for random close packings. In polydisperse dispersions (as in Fig. 1f for instance), jamming sets in at higher packing fractions $\phi_c > 0.64$ [3–5].

If the film thickness h is not negligible compared to the particle radius R , long range forces (van der Waals attraction, screened Coulomb repulsion) have an impact on the shape of the particles. They can be non-spherical for $\phi < \phi_c$: Even though neighboring particles do not touch in this case, flat facets are formed to decrease the intermolecular potential energy at the cost of interfacial energy [7]. To capture interactions between neighboring particles transmitted by long range forces, an effective volume fraction ϕ_{eff} is introduced which is larger than ϕ . It is often estimated to first order in h/R as: $\phi_{eff} \approx \phi(1 + 3h/(2R))$ [8]. For foams or emulsions stabilized by charged surfactants with screened electrostatic repulsion, the thickness h is typically of the order of 5–20 nm [9]. The exact determination of h for a given ϕ requires the minimization of the total free energy [7]. The difference between ϕ_{eff} and ϕ can become large in the case of nano emulsions. As a consequence, the jamming packing fraction is predicted to be a decreasing function of droplet size, in agreement with experimental evidence [7].

Attractive interactions can also affect the shape and packing of the particles. When the suspending liquid contains a surfactant concentration c much larger than the critical micellar concentration (cmc), a short range attraction arises due to depletion forces. The interaction

energy (typically $(10\text{--}40) k_B T$) is strong enough to stick particles together so that packing structure and rheology are significantly modified [10,11]. Alternatively, adhesion between neighboring droplets can be promoted by ligands which connect receptor molecules adsorbed on each water–oil interface [6] (Fig. 1e). Minimization of the total emulsion free energy including the long range interaction potential energy, the interfacial energy and adhesion energy allows the thickness and the radius of the contact films to be predicted [6].

The interfaces in foams and emulsions can not only be stabilized by surfactants, but also by solid particles or by proteins [12–14], widely encountered in food products and research. The adsorbed macromolecules or solid particles form densely packed layers at the interfaces that contribute to steric stabilization of the thin films in addition to the electrostatic repulsion whose magnitude depends on the isoelectric point (often tuned by the pH) [13]. The formation of adsorbed macromolecular or nanoparticle networks across the films can also lead to steric repulsion [15,12]. However, a quantitative description of these interactions is still missing [13].

The structure of foams and emulsions is metastable. It evolves with time due to drainage, coarsening (also known as Ostwald ripening in dilute emulsions), or coalescence [1,16,8]. In emulsions, drainage (also called gravitational syneresis) can be minimized if the densities of both phases are matched. In foams, drainage can be eliminated in microgravity [17], or by using a continuous phase which has a yield stress. Coarsening in foams and emulsions arises from diffusion of the chemical species of the dispersed phase between neighboring particles, driven by Laplace pressure differences. Such differences are reduced in monodisperse foams or emulsions which can be produced with microfluidic devices [18–21]. In any case, coarsening leads to a growth of the average particle diameter with time, accompanied by intermittent structural rearrangements [1]. However, for similar droplet and bubble sizes, coarsening in emulsions is generally much slower than in foams, due to differences of internal phase density and solubility in the continuous phase. Therefore, emulsions with sub-micron sized droplets can be stable over months in contrast to foams where bubbles

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