

Theoretical Model of Viscous Friction inside Steadily Sheared Foams and Concentrated Emulsions

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Abstract. We present briefly a theoretical model of viscous friction in foams and concentrated emulsions, subject to steady shear deformation. In this model we calculate (1) energy dissipated inside the planar films between two neighboring bubbles/drops, which slide along each other dragged by the flow, and (2) energy dissipated on the surface of the bubbles/drops, as a result of their deformation in the flow. Next, from the calculated dissipated energy we determine the macroscopic viscous stress of the sheared foam/emulsion. The model predictions agree well with various experimental data.

INTRODUCTION

The rheological properties of foams and emulsions, with volume fraction of the dispersed phase $\Phi > \Phi_{CP}$ (where Φ_{CP} is the volume fraction of closely packed spheres), are usually described by the Herschel-Bulkley constitutive equation, $\tau = \tau_0 + \tau_v = \tau_0 + k \dot{\gamma}^n$. Here $\dot{\gamma}$ is shear rate, τ is total stress, $\tau_v(\dot{\gamma})$ is its rate-dependent part, τ_0 is yield stress, n is power-law index, and k is consistency. The rate-dependent term, $\tau_v(\dot{\gamma})$, related to the viscous dissipation of energy in the flowing foam/emulsion, is not well understood. Various values of n and k were measured [1-6] or theoretically calculated [2,7-9], without clear understanding why and how they depend on the specific conditions.

Recently, we developed a theoretical model of the viscous friction in steadily sheared foams and concentrated emulsions [10,11]. Here we briefly summarize the main results from our model and its comparison with experimental data.

VISCOUS FRICTION IN THE PLANAR FILMS

We consider foams and concentrated emulsions with volume fraction $\Phi > \Phi_{CP}$. Characteristic feature of these systems is that the drops and bubbles are compressed against each other due to their high volume fraction, so that planar foam/emulsion films are formed, see Fig. 1. For brevity, in the model description below we discuss explicitly only bubbles in foams. However, the model is equally applicable to emulsions and could be upgraded to other types of dispersions of soft particles, such as suspensions of vesicles or gel particles.

For simplicity, we assume that the foam contains monodisperse bubbles, each with volume, $V_B = (4/3)\pi R_0^3$, and these bubbles are arranged in ordered fcc-structure with given Φ , Fig. 1. By considering the relative motion and the viscous friction inside the foam film, formed between two neighboring bubbles in the sheared foam, we calculated the instantaneous film thickness, $h(t)$, and film radius, $R_F(t)$, in the process of bubble-bubble collision [11]. To describe the liquid flow in the film we used the lubrication equation and assumption for tangentially immobile film surfaces (due to high viscosity of the emulsion drops or to surface Marangoni stress created by surfactants). After calculating the film thickness, $h(t)$, we calculated the energy dissipation rate as a result of the viscous friction inside the foam films, formed between the neighboring bubbles. Next, by equalizing the time-averaged energy dissipation rate in the foam (per unit foam volume) with the product of the foam viscous stress and the shear rate, $\langle \dot{E} \rangle = \tau_{VF} \dot{\gamma}$, we derived the following explicit expression for the foam viscous stress, created by friction in the foam films [10]:

$$\tilde{\tau}_{VF} \approx 0.806Ca^{0.465}\Phi^{5/6}/(1-\Phi)^{0.5} \quad (1)$$

where $\tilde{\tau}_{VF} = \tau_{VF}R_0/\sigma$ is the respective dimensionless viscous stress. Therefore, the model predicts that the viscous stress is approximately proportional to $Ca^{1/2}$ (i.e., $n \approx 1/2$), as observed experimentally in various studies [1,6,8]. Here $Ca = (\mu\dot{\gamma}R_0/\sigma)$ is capillary number and μ is viscosity of the continuous phase.

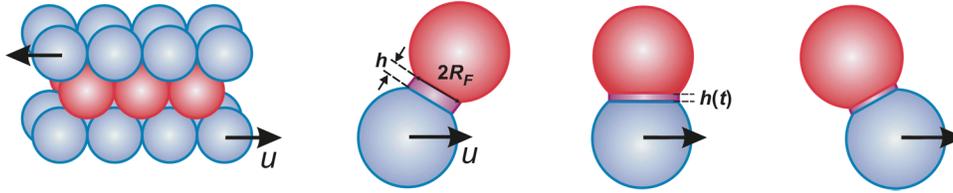


FIGURE 1. Schematic presentation of the relative motion of neighboring planes of bubbles in sheared foam, and of the process of film formation and thinning between two bubbles, sliding along each other, as a result of the flow drag.

Equation (1) should be used in its range of validity only. Extrapolation to $\Phi \rightarrow 1$ is not justified, because the films become very thin at high volume fractions (due to high capillary pressure, which drives the film thinning) and the surface forces between the film surfaces (which could be expressed via the so-called “disjoining pressure”) become important [11]. Therefore, the upper limit of using Eq. (1) is set by the comparison of the thickness of dynamic foam films in sheared foam, $h \approx Ca^{1/2}R_0/4$, with the range of surface forces (typically between 1 and 10 nm) [11]. The lower limit of Φ is set mainly by the model assumption that the bubbles form planar films while sliding along each other [11]. The comparison of the model predictions with experimental data (see Fig. 2 below) shows that Eq. (1) is applicable at least in the range $0.80 < \Phi < 0.98$.

We developed an extended version of the model, in which we account also for (a) friction in the curved meniscus regions surrounding the foam films, and (b) effect of surface forces [11]. Friction in the meniscus region around the films becomes significant only at both high capillary number, ca. $Ca > 10^{-4}$, and low air volume fraction, $\Phi < 0.93$. Surface forces are usually insignificant for steadily sheared foams (except for micrometer-sized bubbles and/or at very low shear rates), because the dynamic films in these systems are typically thicker than the range of surface forces. In contrast, for micrometer-sized drops and bubbles, the surface forces could be important, because their range becomes comparable to the dynamic film thickness. The calculations showed that significant surface forces lead to stronger dependence of τ_v on Ca (viz. $1/2 < n < 1$) [11].

Let us compare now the model predictions with the experimental results of Princen and Kiss [1], who measured the viscous stress, $\tau_v(Ca)$, for series of concentrated emulsions with different Φ . The comparison showed a reasonably good agreement with all experimental data without using adjustable parameters - no difference larger than 25 % was found (for most of the data < 10 %). As illustration, we show in Fig. 2(a) our theoretical curves and the experimental data for two of the samples studied in [1].

Next, we compare the model predictions with experimental results for sheared foams, obtained by us with the procedure from ref [6]. This comparison also showed reasonably good agreement without adjustable parameter for foams, stabilized by synthetic surfactants, see as example the lowest curve in Fig. 2(b). Additional results demonstrating the agreement of Eq. (1) with experimental data, obtained by us with emulsions and foams, are shown in [11] (again without adjustable parameters).

The upper two curves in Fig. 2(b) could not be explained by Eq. (1), because they evidence much higher overall energy dissipated in the foams, as compared to the energy dissipated in the respective foam films. Characteristic feature of these “high-friction” foaming systems is their very high surface dilatational modulus, $G_D > 100$ mN/m, which is related to the presence of specific cosurfactants (myristic acid and lauric acid) in the foaming solutions. These results indicate that the surface dissipation of energy on the bubble surface could be important for such systems. To account for this effect, in Ref. [11] we approximated the consecutive expansions and contractions of the bubble surface in the shear flow (due to the collisions with the neighboring bubbles) with oscillatory deformation of amplitude, δS , and estimated the contribution of the resulting surface dissipation to the total dissipated energy in the sheared foam. Thus we were able to derive the following expression for the contribution of the surface dissipation of energy into the total viscous stress [11]:

$$\tilde{\tau}_{VS} \equiv \tau_{VS}R_0/\sigma \approx 9.8\pi(G_{LS}/\sigma)\Phi(\delta \ln S)^2 \quad (2)$$

where G_{LS} is surface loss modulus. Taking for estimates $\Phi = 0.9$ and relative amplitude of surface expansion/contraction $\delta \ln S = \delta S/S_0 \approx 1$ %, we obtained for the dimensionless stress $\tilde{\tau}_{VS} \approx 2.8 \times 10^{-3}G_{LS}/\sigma$, which

shows that (a) $\tilde{\tau}_{vs}$ could be important, if the surface loss modulus is sufficiently high, and (b) this contribution should be a weak function of the capillary number, only via possible dependences of $\delta \ln S$ and G_{LS} on Ca . These features agree well with the experimental results obtained with foams stabilized by various types of surfactants [11]. As illustration, in Fig. 2(b) we compare theoretically calculated total viscous stress, $\tilde{\tau}_v = \tilde{\tau}_{vF} + \tilde{\tau}_{vs}$, with the experimental data from foam studies, by using an empirical power-law fit of the product entering Eq. (2), $(G_{LS}/\sigma)(\delta \ln S)^2 = A \dot{\gamma}^{0.18}$, where $A \approx 12.6$ for foams containing lauric acid (LAc) and $A \approx 21.2$ for foams containing myristic acid (MAc) are constants determined from the fit. These values of A are rather reasonable - for $\delta \ln S \approx 1\%$ and $\dot{\gamma} = 0.2 \text{ s}^{-1}$, they give $G_{LS} \approx 240 \text{ mN/m}$ for LAc and $G_{LS} \approx 400 \text{ mN/m}$ for MAc, respectively, which was very close to the experimental values, measured with the foaming solutions by the oscillating drop method [11]. Thus we can conclude that the viscous dissipation of energy at the bubble surface is responsible for the high viscous stress, measured with foams containing LAc and MAc as cosurfactants [11] and that $n < 1/2$ in such systems.

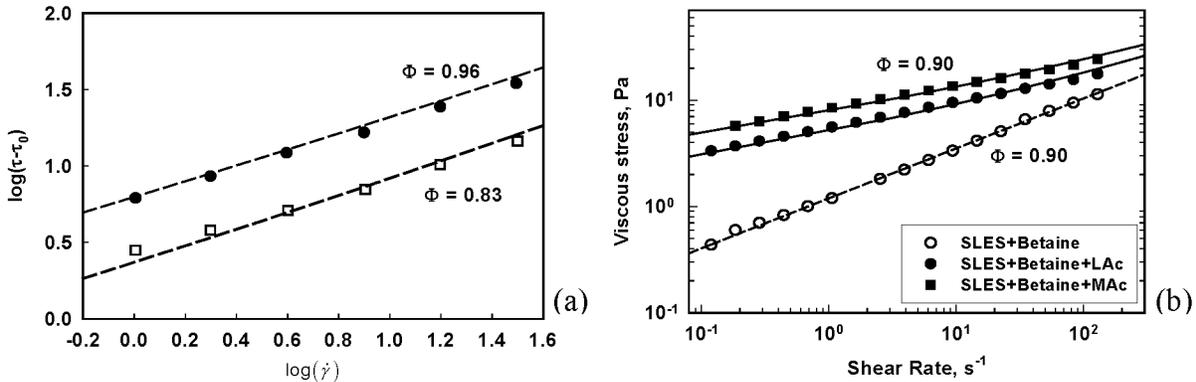


FIGURE 2. Comparison of model predictions (curves) with experimental results (symbols): (a) Oil-in-water emulsions with $\Phi = 0.83$ and 0.96 [1]; (b) Foams and emulsions stabilized with various surfactants, $\Phi = 0.90$.

In conclusion, our model predicts that the macroscopic viscous stress is approximately proportional to $Ca^{1/2}$, i.e. the power-law index $n \approx 1/2$, when the contributions of the surface dissipation of energy and of the disjoining pressure, acting in the films between the sliding bubbles/drops, are both negligible [10]. The model predictions are compared with experimental data and a very good agreement is found without adjustable parameters for both emulsions and foams. The account for the surface dissipation of energy on the bubble surfaces predicts $n < 1/2$, whereas the disjoining pressure leads to $n > 1/2$ [11], thus explaining why different values of n are measured in various studies.

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