

Viscous Friction in Foams and Concentrated Emulsions under Steady Shear

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(Received 30 April 2007; revised manuscript received 6 January 2008; published 3 April 2008)

We present a model for the viscous friction in foams and concentrated emulsions, subject to steady shear flow. First, we calculate the energy dissipated due to viscous friction inside the films between two neighboring bubbles or drops, which slide along each other in the flow. Next, from this energy we calculate the macroscopic viscous stress of the sheared foam or emulsion. The model predictions agree well with experimental results obtained with foams and emulsions.

DOI: [10.1103/PhysRevLett.100.138301](https://doi.org/10.1103/PhysRevLett.100.138301)

PACS numbers: 83.80.Iz, 47.57.Bc, 82.70.Kj, 82.70.Rr

The rheological properties of foams and concentrated emulsions, with a volume fraction of the dispersed phase $\Phi > \Phi_{CP}$ (where Φ_{CP} is the volume fraction of closely packed spheres), are usually described [1–7] by the Herschel-Bulkley equation, $\tau = \tau_0 + \tau_V(\dot{\gamma}) = \tau_0 + k\dot{\gamma}^n$. 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. Theoretical and experimental studies showed that τ_0 scales with the capillary pressure of the bubbles or drops and depends on Φ [1–5,9,10]. The rate-dependent term $\tau_V(\dot{\gamma})$, related to the viscous dissipation of energy, is not well understood. Various values of n and k were measured [1–6] or estimated [2,11–13] without a clear understanding of why and how they depend on specific conditions.

In this Letter we describe a simple theoretical model of the viscous friction in steadily sheared foams and concentrated emulsions. In such systems, drops and bubbles are compressed against each other due to their high volume fraction, so that planar foam or emulsion films are formed. For brevity, in the model formulation we discuss explicitly only bubbles in foams. However, the model is equally applicable to emulsions (unless the drop viscosity is so high that the drop deformation time is comparable to $1/\dot{\gamma}$) and could be upgraded to other types of dispersions of soft particles, such as suspensions of vesicles and gel particles.

The current model differs from the other rheological models proposed in literature in several aspects: First, we consider steadily sheared foam, in which foam films are perpetually forming and disappearing between the bubbles, which slide along each other dragged by the flow. The bubble dynamics in such foams is qualitatively different from the case of small oscillatory deformations of the foam around its equilibrium configuration. Therefore, the models of the oscillatory deformation [2,11,12] are inapplicable to describe the steady foam flow. Second, we are interested in shear rates characterizing the foam or emulsion transportation (ca. 0.1 to 200 s^{-1}). Hence, we assume that bubble size and volume fraction are known, and we do not consider Ostwald ripening and water drainage, which

are important at longer time scales [5,14–17]. Third, we assume that the main viscous friction occurs in planar films formed between sliding bubbles. Hence, the current model is applicable only to foams with volume fraction $\Phi > \Phi_{CP}$ and could not be compared to models and experimental results obtained at $\Phi < \Phi_{CP}$ [3,4,18,19].

We developed an extended version of our model, in which we account also for the friction in the Plateau borders (PBs) surrounding the films and for the surface dissipation at bubble surface. Numerical estimates by the extended model showed that the friction in PBs is detectable, but usually smaller than the friction in foam films—below 30% for all systems considered in the current manuscript, except for the data at the highest capillary numbers, $Ca = 10^{-3}$, where the contribution of PBs increases to $\approx 50\%$. The extended model predicts that surface dissipation is important for systems with high surface modulus, E_S , in good agreement with the experimental results in [6], where foams stabilized by different surfactants were studied and much higher viscous stress was measured when fatty acid salts with $E_S > 100$ mN/m were used (compared with < 5 mN/m for typical synthetic surfactants). Because of limited space, we present the basic model and comparison with experimental data in this Letter, while the extended model is presented in subsequent study [20].

For simplicity, we assume that the static foam contains monodisperse bubbles arranged in an fcc lattice, with given Φ and bubble volume, $V_B = (4/3)\pi R_0^3$. The distance between the centers of two neighboring bubbles is $l_S \approx 1.812R_0/\Phi^{1/3}$, where the numerical factor is calculated for bubbles with the shape of rhombic dodecahedron (for other shapes this factor is similar within a few percent). The film radius R_{FS} can be estimated from expressions derived by Princen [21,22], $R_{FS} = (4S_F/pS)^{1/2}R_0$, where $p = 12$ is the number of planar films per bubble, $S_F(\Phi)$ is the area of the bubble surface occupied by films, and $S(\Phi)$ is the total surface area of the deformed bubble. From Princen's approach one can determine also the capillary pressure of the bubbles, $P_C(\Phi) = 2\sigma S\Phi/R_0S_0[\Phi - f(\Phi)]$, where σ is interfacial tension and $S_0 = 4\pi R_0^2$ is

the area of the nondeformed bubbles. Explicit expressions for the functions $S_F(\Phi)$, $S(\Phi)$, and $f(\Phi)$ are given in [22]. Thus we determine the geometrical parameters of the deformed bubbles in the static foam and the bubble capillary pressure $P_C(\Phi)$ which are needed in the following consideration.

We consider now the viscous friction between two bubbles located in two neighboring planes of the assumed fcc structure of the foam. These planes are assumed to slide with constant velocity u along each other in the sheared foam; see Fig. 1. The relative position of the bubbles can be described by the distance between their geometrical centers, $l(t) = [l_m^2 + (ut - x_0)^2]^{1/2}$, or by the angle $\alpha(t)$, where $\sin\alpha(t) = l_m/l(t)$ [23]. Here $l_m = l_S\sqrt{3}/2$ is the minimal distance between the bubble centers, $x_0 = (l_0^2 - l_m^2)^{1/2}$, and $l_0 = l(t=0)$ is the distance in the moment of film formation.

The sliding bubbles form a transient foam film with radius $R_F(t)$. For convenience we introduce an effective radius of the deformed bubbles, $R_{\text{EFF}} = (R_{FS}^2 + l_S^2/4)^{1/2}$, defined as the radius of a spherical surface with just one film (instead of the 12 films in the fcc structure) that has the same ratio R_{FS}/l_S , as the deformed bubbles in the real foam. Thus we replace the real polyhedral bubbles by “imaginary” bubbles having just one film, and the instantaneous film radius becomes $R_F(t) = [R_{\text{EFF}}^2 - l(t)^2/4]^{1/2}$.

To describe the liquid flow in the film between the bubbles, we use the lubrication equation ($dP/dr = \mu[\partial^2 V_r(r, z)/\partial z^2]$), written in a radial r - z -coordinate system (located in the center of the film with z axis perpendicular to the film plane); μ is liquid viscosity, and $P(r)$ is pressure in the film [24,25]. Assuming tangentially immobile bubble surfaces (due to high viscosity of the emulsion drops or to surface Marangoni stress created by surfactants), the boundary conditions for the fluid velocity at the film surfaces are $V_r(r, z = \pm h/2) = \mp u \sin\alpha(t) \cos\varphi/2$, where $h(t)$ is the instantaneous film thickness, $u \sin\alpha(t) \cos\varphi$ is the projection of the relative bubble velocity in the plane of the film, and φ is polar angle in the film plane. By using standard procedures, one can show that the film thinning is governed by the known Reynolds equation [24]:

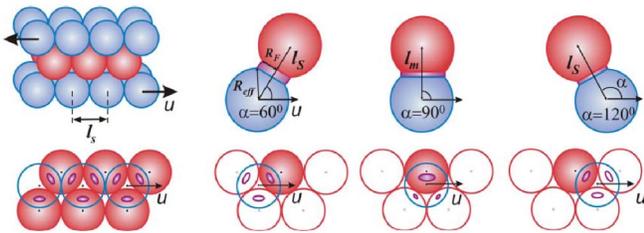


FIG. 1 (color online). Schematic presentation of the relative motion of neighboring planes of bubbles in sheared foam, and of the process of film formation between two bubbles, sliding along each other (upper line: side view; bottom line: projection onto the plane of bubbles).

$$(dh/dt) = -2[P_C - \Pi(h)]h^3/3\mu R_F^2. \quad (1)$$

Here $\Pi(h)$ is the disjoining pressure accounting for the surface forces between the two film surfaces (electrostatic, van der Waals, etc. [25]). For simplicity, we neglect below the surface forces $\Pi(h) \ll P_C$, although they can be incorporated straightforwardly in the calculations [20]. Using the fact that $h \ll l$, one can integrate Eq. (1) to obtain an explicit expression for the film thickness $h(t)$:

$$\frac{1}{h^2} = \frac{1}{h_0^2} + \frac{16P_C}{3\mu} \frac{1}{u\sqrt{4R_{\text{EFF}}^2 - l_m^2}} \left[\operatorname{arctanh}\left(\frac{\sqrt{l_0^2 - l_m^2}}{\sqrt{4R_{\text{EFF}}^2 - l_m^2}}\right) + \operatorname{arctanh}\left(\frac{ut - \sqrt{l_0^2 - l_m^2}}{\sqrt{4R_{\text{EFF}}^2 - l_m^2}}\right) \right], \quad (2)$$

where $h_0 = h(t=0)$ is the film thickness in the moment of film formation.

From the lubrication equation, one derives the following expression for the fluid velocity in the film, which is used below to calculate the dissipated energy:

$$\begin{aligned} V_r(r, z) &= -2P_C r(z^2 - h^2/4)/\mu R_F^2 - u \sin\alpha(t) z \cos\varphi/h, \\ V_\varphi(r, z) &= u \sin\alpha(t) z \sin\varphi/h. \end{aligned} \quad (3)$$

For the calculation scheme we should specify the initial moment of collision between the bubbles (viz., the moment of planar film formation) and the respective quantities, such as h_0 , R_{F0} , l_0 , etc. Following [24], we assume that the planar foam film is formed when the dynamic pressure in the gap between the colliding bubbles becomes comparable to bubble capillary pressure $P(r=0) \approx P_C$. As shown in [24], this condition leads to the following expression for the initial film thickness, $h_0 = F/2\pi\sigma$, where F is the force pushing the bubbles against each other. At low Reynolds number, this pushing force could be estimated by Taylor’s formula, $F = 3\pi\mu R_N^2 u_z/2h$, where R_N is the radius of curvature of the approaching bubble surfaces and $u_z(t) = u \cos\alpha(t)$ is the velocity component along the line connecting bubble centers. Thus we obtain $h_0 = [(3/4)\cos\alpha_0 \tilde{u}]^{1/2} R_N$, where $\alpha_0 = \alpha(t=0)$ is the angle in the moment of film formation and $\tilde{u} = (\mu u/\sigma)$ is the dimensionless relative velocity of the two neighboring bubble planes in the foam. We assume that R_N is approximately equal to the radius of curvature of the nodes in the static foam, $R_N = 2\sigma/P_C$, where $P_C(\Phi)$ is known [22]. The force balance shows [24] that the initial film radius is $R_{F0} = (h_0 R_N)^{1/2}$, and the distance between bubble centers in the moment of film formation is $l_0 = 2[R_{\text{EFF}}^2 - R_{F0}^2]^{1/2}$. Thus we obtained a complete set of equations for the foam film formation and thinning between two neighboring bubbles in sheared foam.

The rate of energy dissipation inside the foam film is

$$-\frac{dE_{\text{DF}}}{dt} = \mu \int_0^{2\pi} \int_0^{R_F} \int_{-h/2}^{h/2} \left[\left(r \frac{\partial}{\partial r} \left(\frac{V_\varphi}{r} \right) + \frac{1}{r} \frac{\partial V_r}{\partial \varphi} \right)^2 + \left(\frac{\partial V_\varphi}{\partial z} \right)^2 + \left(\frac{\partial V_r}{\partial z} \right)^2 \right] r dz dr d\varphi, \quad (4)$$

where the subscript ‘‘DF’’ denotes dissipation inside the films. To determine the energy dissipated inside one foam film, $\tilde{E}_{\text{DF}} = E_{\text{DF}}/(R_0^2 \sigma \tilde{u}^{1/2})$, we integrate Eq. (4) over the contact time of the two bubbles to derive [see also Eqs. (3)]:

$$\tilde{E}_{\text{DF}} = - \int_0^{\tilde{t}_{\text{END}}} \left(\frac{8\pi}{3} \frac{[\eta(\tilde{t})]^3}{\xi_N^2} + \pi [\sin \alpha(\tilde{t})]^2 \frac{[\xi_F(\tilde{t})]^2}{\eta(\tilde{t})} \right) d\tilde{t}, \quad (5)$$

where the dimensionless quantities $\xi_N = R_N/R_0$, $\xi_F = R_F/R_0$, $\tilde{t} = tu/R_0$, and $\eta = h/h_C$ are introduced, where $h_C \equiv \tilde{u}^{1/2} R_0$ is the scaling factor for the film thickness. The scaling for h is chosen to comply with the dependence $1/h^2(\alpha \approx \pi/2) \propto \sigma/\mu u = 1/\tilde{u}$, predicted by Eq. (2), in which the term with h_0 is negligible and the second term in the brackets is identically zero at $\alpha = \pi/2$. This particular scaling leads to numerical values of \tilde{E}_{DF} , which depend very weakly on the relative bubble velocity, $\tilde{E}_{\text{DF}} \propto \tilde{u}^{-0.035}$.

Next, we determine the time-averaged energy dissipation rate per unit foam volume $\langle \dot{E} \rangle$, which is equal to the macroscopic viscous stress τ_{VF} multiplied by the shear rate $\dot{\gamma}$. The shear rate and the conventional capillary number $\text{Ca} \equiv (\mu \dot{\gamma} R_0/\sigma)$ are proportional to the relative velocity of the bubble planes, $\dot{\gamma} = u/m$ and $\text{Ca} = \tilde{u} R_0/m \approx 0.676 \tilde{u} \Phi^{1/3}$, where $m(\Phi) = (2/3)^{1/2} l_S \approx 1.479 R_0/\Phi^{1/3}$ is the distance between the planes. To find $\langle \dot{E} \rangle$, we consider the motion of the bubble plane as a sequence of equivalent steps with length l_S . During one such step, the six contacts of the ‘‘central’’ bubble with its neighbors undergo partial cycles of type ‘‘film formation-thinning-disappearance,’’ like those expressed by Eq. (5). Geometrical consideration shows that these partial cycles could be summed up to 4 equivalent full friction cycles. Thus, the viscous stress of the foam is

$$\begin{aligned} \tau_{\text{VF}} \dot{\gamma} &= \langle \dot{E} \rangle \\ &= \frac{1}{2} (4E_{\text{DF}} \Phi / V_B t_C) \\ &= 2E_{\text{DF}} \Phi u / V_B l_S \\ \Rightarrow \tilde{\tau}_{\text{VF}} &= \tau_{\text{VF}} / (\sigma / R_0) \\ &= 0.39 \tilde{u}^{1/2} \Phi \tilde{E}_{\text{DF}} \\ &\approx 0.474 \text{Ca}^{1/2} \Phi^{5/6} \tilde{E}_{\text{DF}}, \end{aligned} \quad (6)$$

where the multiplier 1/2 accounts for the sharing of the dissipated energy inside one film by two neighboring bubbles, and $\tilde{\tau}_{\text{VF}}$ is the respective dimensionless stress. The subscript ‘‘VF’’ denotes viscous friction inside foam films. The respective dimensionless effective viscosity of the foam is $\tilde{\mu}_{\text{EF}} \equiv \mu_{\text{EF}}/\mu = \tilde{\tau}_{\text{VF}}/\text{Ca} \approx 0.474 \Phi^{5/6} \text{Ca}^{-1/2} \tilde{E}_{\text{DF}}$. Therefore, the model predicts that the viscous stress is approximately $\propto \text{Ca}^{1/2}$, whereas $\mu_{\text{EF}} \propto \text{Ca}^{-1/2}$, just as observed experimentally in [1]. This scaling is ultimately related to the dependence $h \propto \text{Ca}^{1/2}$, predicted by Eq. (2) as explained above.

To account more precisely for the effects of Φ and Ca , we calculated numerically \tilde{E}_{DF} in the ranges $10^{-6} \leq \text{Ca} \leq 10^{-2}$ and $0.80 \leq \Phi \leq 0.99$. The numerical results were fitted by empirical function, $\tilde{E}_{\text{DF}} = 1.7 \text{Ca}^{-0.035} / (1 - \Phi)^{0.5}$, which was combined with Eq. (6) to obtain the final model expression for the contribution of the friction in the foam films into the foam viscous stress

$$\tilde{\tau}_{\text{VF}} \approx 0.806 \text{Ca}^{0.465} \Phi^{5/6} / (1 - \Phi)^{0.5}. \quad (7)$$

Equation (7) 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) and the surface forces, which were neglected here, become important [20]. Therefore, the upper limit of using these equations is set by the comparison of the thickness of the dynamic films, $h \approx 0.2 h_C \approx \text{Ca}^{1/2} R_0/4$, with the range of surface forces (typically between 1 and 10 nm). The lower limit of Φ is set mainly by the model assumption that the bubbles form planar films while sliding along each other [19]. The comparison of the

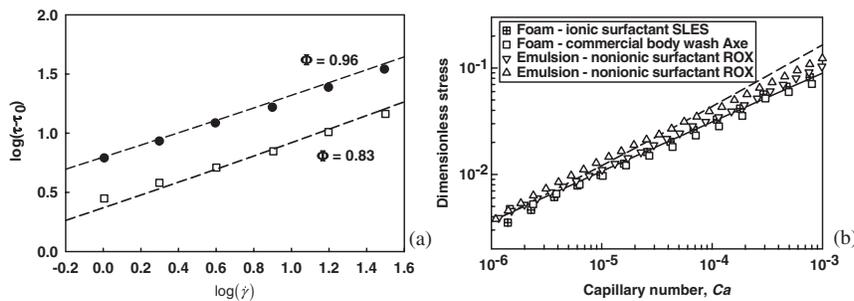


FIG. 2. Comparison of model predictions with experimental results (symbols): (a) oil-in-water emulsions with $\Phi = 0.83$ and 0.96 [1]; (b) foams and emulsions stabilized with synthetic surfactants. The solid curve in (b) is drawn according to Eq. (7), whereas the dashed curves are drawn with account for the dissipation in plateau borders (all curves—without adjustable parameter).

model predictions with experimental data (see Fig. 2 below) shows that Eq. (7) is applicable at least in the range $0.80 < \Phi < 0.98$.

Let us compare model predictions with the experimental results of Princen and Kiss [1], who measured the viscous stress, $\tau_V(\text{Ca})$, for a series of concentrated emulsions with different Φ . The comparison showed a reasonably good agreement with all experimental data without using any adjustable parameter—no difference larger than 25% was found (for most of the data $< 10\%$). In Fig. 2(a) we show as illustration 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 and emulsions, obtained by us with the procedure from Ref. [6]. This comparison also showed reasonably good agreement without adjustable parameter for both foams and emulsions, stabilized by various synthetic surfactants; see Fig. 2(b).

Note that the procedure used for comparing the model with experiment (assuming $\tau_V = \tau - \tau_0$) implies that the elastic contribution to total stress in sheared foam is a weak function of $\dot{\gamma}$. This assumption is strongly supported by the fact that our model describes equally well both foams and emulsions, for which the relative contribution of the elastic term is rather different (higher for emulsions due to the smaller drop size, as compared to bubbles in foams). If the elastic term was contributing significantly to the rate-dependent part of τ , one should expect different dependences $\tau_V(\dot{\gamma})$ for foams and emulsions, which is not observed with the systems studied.

In conclusion, we present a theoretical model for the viscous friction inside foams and concentrated emulsions, subject to steady shear. The model predicts that the macroscopic viscous stress is approximately proportional to $\text{Ca}^{1/2}$, when the contributions of the disjoining pressure $\Pi(h)$ between the surfaces of the sliding bubbles or drops and of the surface dissipation are negligible. The model predictions are compared with experimental data and a very good agreement is found without adjustable parameters for both emulsions and foams.

As shown in a related study [20], the effect of Π leads to stronger dependence of τ_V on Ca ($1/2 < n < 1$), whereas the surface dissipation and possible shear thinning of the continuous phase lead to $n < 1/2$. These extensions of the current model explain why different values of n are also found experimentally.

Let us note that our model could be upgraded to other types of dispersions of soft particles, such as suspensions of vesicles and gel particles, for which similar scaling of the viscous stress with $\text{Ca}^{1/2}$ was reported [26,27]; see, e.g., [26] for a possible approach. Therefore, the model makes a link between the rheological properties of all these systems (emulsions or foams, gel particles, vesicles), which are usually studied by independent research communities.

This study is supported by Unilever GRC, Trumbull, CT. We are grateful to Professor I.B. Ivanov and Dr. V. Subramanian for useful discussions.

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