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Shear and dilational interfacial rheology of surfactant-stabilized droplets ☆

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ABSTRACT

A new measurement method is suggested that is capable of probing the shear and dilational interfacial rheological responses of small droplets, those of size comparable to real emulsion applications. Freely suspended aqueous droplets containing surfactant and non-surface-active tracer particles are transported through a rectangular microchannel by the plane Poiseuille flow of the continuous oil phase. Optical microscopy and high-speed imaging record the shape and internal circulation dynamics of the droplets. Measured circulation velocities are coupled with theoretical descriptions of the droplet dynamics in order to determine the viscous (Boussinesq) and elastic (Marangoni) interfacial effects. A new Marangoni-induced stagnation point is identified theoretically and observed experimentally. Particle velocimetry at only two points (including gradients) in the droplet is sufficient to determine the amplitudes of the dilational and shear responses. We investigate the sensitivity for measuring interfacial properties and compare results from droplets stabilized by a small-molecule surfactant (butanol) and those stabilized by relatively large block copolymer molecules. Future increased availability of shear and dilational interfacial rheological properties is anticipated to lead to improved rules of thumb for emulsion preparation, stabilization, and general practice.

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1. Introduction

Surfactants are added to fluids in order to modify interfacial properties: reduce interfacial tension, induce Marangoni elasticity, and introduce viscoelastic properties to the interface. Such changes have dramatic impact on emulsion properties. They make or break emulsion stability. Of these properties, interfacial rheology is the least studied, yet it is known to significantly retard droplet coalescence [1,2]. Improved measurement techniques for interfacial rheology should advance understanding of its effect on emulsion performance. Here we suggest a new interfacial rheology method that tests small droplets directly, those of size comparable to real emulsion applications.

Interfacial rheology [3] is challenging theoretically and experimentally; theoretically, the boundary conditions at the interface are complex (including shape, motion, tension, and surfactant concentration) and unknown *a priori*. Experimentally, dilational and shear properties are both relevant, yet not readily accessible [4]. Generally, different techniques are required for each property: ring [5], needle [6,7], and bicone [8] geometries for shear; and pendant droplet, capillary wave, and Wilhelmy techniques for dilation [9,10].

To examine small droplets, microfluidic technology presents various advantages. Microfluidic devices offer rapid, steady droplet production, and multiple fluid inlets allow for high-throughput capability. Furthermore, the channel geometry can be altered easily to prescribe the desired flow. In past work, microfluidic devices similar to those employed here were used to measure the interfacial tension of multicomponent immiscible liquids [11] and probe mass transport and interfacial kinetics from droplets during a liquid-phase extraction process [12].

A suspended droplet in flow travels at a velocity that is intermediate to neighboring velocities in the surrounding fluid, thus causing the droplet fluid to circulate. Due to the spherical nature of droplets, the natural language for their internal circulation and interfacial dynamics is vector spherical harmonics, which importantly form two types: an area element on the surface of the sphere deforms either with or without changing area. Dilational types of course involve contraction or expansion of an area element, whereas shear types involve only a change in shape. By flowing droplets through a microchannel, we excite behavior of

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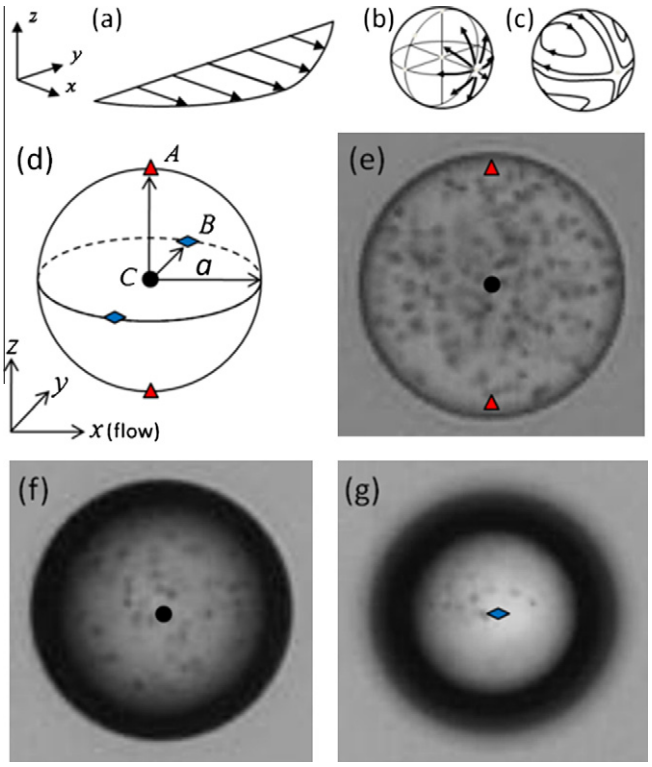

Fig. 1. Experimental geometry to measure the internal circulation of a droplet (radius, a) by particle velocimetry. (a) A plane Poiseuille flow (with velocity along x and velocity gradient along y) is set up within a rectangular microchannel. A droplet in the center of this flow samples different flow rates in its surroundings, and internal circulation patterns are established. These are (b) dilational (area-compressible), where fluid in the center of the droplet advances to the leading nose and returns to the rear about the periphery, and (c) shear (area-incompressible), where the interface experiences only shear and the fluid in the center is motionless (illustrated schematically here in the droplet frame of reference). (d) Velocimetry is carried out primarily at three points: A–C. The viewpoint for the following images is in the y-direction. (e) Image of the x–z mid-plane ($y = 0$) of a water/ethylene glycol droplet ($a = 49$ μm) in silicone oil, an "index-matched" system. (f) Image of the x–z mid-plane ($y = 0$) of a water droplet ($a = 52$ μm) in mineral oil. (g) Image of the x–z plane at the top ($y = -a$) of the water droplet in mineral oil. Note that the droplet edge in (g) is out of focus.

each type (shown schematically in Fig. 1b and c), and their magnitudes directly indicate the respective dilational and shear properties of the interface. For a droplet on the centerline of plane Poiseuille flow (illustrated in Fig. 1a), the circulation relative to the droplet center is a type of fountain flow. Theoretical analysis, described in our recent article [13], concludes that velocimetry at only two points in the droplet is sufficient to determine the amplitudes of the dilational and shear behavior. (A similar analysis of vesicular spherical caps in flow attached to a solid surface also points to this method of measuring interfacial viscosity [14,15].) In this paper, we explore Marangoni effects and demonstrate theoretically that they too can be determined by measuring the velocity gradient at one of these points. We carry out such measurements and compare to new theoretical predictions.

2. Experimental methods

To accomplish these measurements, optical microscopy and high-speed imaging record the shape and internal circulation dynamics of droplets in plane Poiseuille flow through a rectangular microfluidic channel.

2.1. Materials

In this study, solutions of ethylene glycol (from J.T. Baker[4]) and distilled water containing various concentrations of surfactant were prepared for use as the droplet phase; silicone oil (Gelest T22) was used as the continuous phase. The ethylene glycol/water mixtures were prepared in either a 40/60 or a 50/50 mass ratio to achieve a desired refractive index contrast to the silicone oil phase. Two surfactants were investigated: a small-molecule alcohol surfactant – *n*-butanol (Mallinckrodt) at (0.70, 1.7, 3.4, and 6.8)% mass fraction; a diblock copolymer surfactant – poly(dimethyl siloxane-*b*-ethylene oxide) at (0.1 and 1.0) mmol/L concentrations (Polysciences, Inc., 3000 g/mol, 80% mass fraction ethylene oxide). Polystyrene spheres (2 μm diameter, Polysciences, Inc.) were added to the droplet phase in concentrations less than 0.2% mass fraction to serve as tracer particles for the velocimetry measurements. All materials were used as received. The viscosities of the oil and aqueous phases are approximately (200 and 2) mPa s at 23 °C, respectively.

Consistent with these surfactants, we assume that the interface is always fluid. Therefore, our theoretical analysis does not consider solid or viscoelastic material at the interface. At a high enough rate, polymeric surfactants may eventually be viscoelastic, but here the interfacial deformation rates are less than 10 s^{-1}, as noted below.

2.2. Microchannel design

Microfluidic channels were fabricated using soft lithography and poly(dimethylsiloxane) replication as described elsewhere [11,12,16,17]. Microfluidic devices were mounted on an Olympus IX71 inverted microscope fitted with an automated translating XY stage (Prior H107). Fluid was driven by microstepping syringe pumps (New Era), capable of delivering fluid with accuracy better than 0.1%. Aqueous droplets were formed at a *T*-junction and promptly enter the microfluidic channel. There are two inlets for the aqueous phase and several inlets for the oil phase, allowing for control of the droplet position (in three dimensions) and speed in the channel [12]. Because of small variations in the microchannel geometry during fabrication, each microfluidic device formed droplets at different vertical heights in the channel. In order to minimize the difference (y_o) in the position of the droplet mid-plane and the centerline of the channel, precise control of the droplet height was achieved through the injection or withdrawal of continuous phase fluid from an inlet positioned above the microchannel and downstream from the droplet formation zone [12]. This height adjustment was made in order to produce images similar to Fig. 1e and f, in which the microscope is focused on the mid-plane of the channel.

2.3. Interfacial tension measurements

Each experiment involves recording the age, shape, and internal circulation of droplets as they convey near the centerline of a rectangular microfluidic channel. The microchannels used in this study had typical dimensions of 1500 μm width by 300 μm height in the wide portion of the channel, giving an aspect ratio of 5. The channel featured multiple 5:1:5 constriction/expansion zones that facilitated the measurement of the liquid–liquid interfacial tension. Upon entering the constriction, the fluid accelerated and an extensional flow was present on the centerline of the channel. This

[4] Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that these are necessarily the best available for the purpose.