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Transition from Newtonian to non-Newtonian surface shear viscosity of phospholipid monolayers

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The surface shear viscosity of DPPC (dipalmitoylphosphatidylcholine) monolayers on the air/water interface was determined over a wide range of surface concentrations in an annular channel. DPPC is studied widely because it is ubiquitous in biological systems. Brewster angle microscopy (BAM) was found to be capable of measuring the monolayer velocity field, even in the absence of co-existing phase domains. Interfacial velocimetry via cross correlations of BAM images provides accurate and non-invasive measurements, useful for both macro and microrheology. The measured velocity profiles are compared with computed profiles obtained over a range of surface shear conditions using the Boussinesq-Scriven surface model, from which the surface shear viscosity was determined. For monolayers in the liquid expanded (LE) and liquid expanded/liquid condensed (LE/LC) co-existing phases, we observe Newtonian behavior. We also show how the flow departs from the Newtonian regime for monolayers with larger surface concentration, corresponding to LC phase transition to solid phase.

I. INTRODUCTION

Monomolecular films on liquid interfaces are of wide interest for scientific and technological reasons. Aside from the elasticity that they impart on the interface—a direct result of surface tension gradients with varying surface packing—monolayers can make the interface exhibit an “excess” viscosity. For small scale systems the relative effects of surface viscosities become significant compared to those of surface tension gradients, thus surface viscosities must be understood, be it for industrial applications, such as foam manufacturing, or for biological systems, such as the liquid lining in lungs. Quantitative, non-invasive measurement of surface viscosities, accounting for the interaction with the bulk liquid, is a challenge for monolayers on the surface of water.

In a review, McConnell\textsuperscript{1} painted a clear picture of the structure and thermodynamics of lipid monolayers at a quiescent air/water interface. More than twenty years later, a coherent understanding of lipid monolayer hydrodynamics seems to elude us. Controversy prevails over whether such films ever behave Newtonian and if their flow is amenable to treatment by the Boussinesq-Scriven surface model, especially when they exist as condensed phases.\textsuperscript{2} Here, we show a clear delineation between Newtonian and non-Newtonian behavior for the surface shear viscosity of lipid monolayers. For this study we utilize the phospholipid DPPC (dipalmitoylphosphatidylcholine) as a model monolayer. There is a vast body of literature on DPPC films on the surface of water,\textsuperscript{1,3-16} in part because it is the most prevalent component of lung surfactant; DPPC is also ubiquitous in bilayers that form cell walls.

Numerous approaches have been presented for studying the surface shear viscosity of monolayers on liquid surfaces. Some methods require floating an object on the surface and/or involve optical measurements. Among the optical approaches, many require fluorescent dyes which affect the
thermodynamic behavior of the monolayer being investigated. For example, 1% mole of a fluorescent lipid can change the surface pressure of DPPC on water by as much as 30%. Quantifying effects of these dyes on the hydrodynamics is not trivial.

The deep-channel surface viscometer flow geometry (Fig. 1) is established as one of the most sensitive and accurate means for determining the surface shear viscosity. This flow isolates the effects of surface shear viscosity because it is the only interfacial property that appears in the azimuthal component of the tangential stress balance. This is in contrast to planar flows where it is the sum of the surface shear and dilatational viscosities that appears in the tangential stress balance. The coupling between the film and the bulk flow in the deep-channel flow can be analytically taken into account in the inertialess limit. However, inertia can be employed to improve the signal-to-noise ratio, with the added cost of nonlinear computations. When the interaction between the bulk and surface flow is not accounted for properly, non-physical results are sometimes reported, such as negative surface shear viscosity.

In order to non-invasively measure the monolayer velocity profile in the flow apparatus, a method was developed using the cross-correlation of Brewster angle microscope (BAM) images. The surface shear viscosity is subsequently determined by matching the measured velocity profiles to those numerically computed for various surface shear viscosities in the same flow. The direct comparison between the measured and computed velocity profiles also indicates whether or not the monolayer flow is Newtonian.

II. EXPERIMENTAL TECHNIQUES

The deep-channel viscometer geometry utilizes an annular flow region between two stationary cylinders. The monolayer is spread on the surface of the channel and the bottom is set to rotate at a constant angular velocity $\Omega$ (rad s$^{-1}$). For this study we utilized an optically accessible channel. The inner and outer cylinder radii are $r_i = 7.62$ cm and $r_o = 9.82$ cm, the depth of the water is $h = 1.1$ cm, the kinematic viscosity of the water (pure, at 22 °C) is $v = 9.57 \times 10^{-3}$ cm$^2$/s, and its density is $\rho = 0.998$ g/cm$^3$.

Brewster angle microscopy was utilized to measure the flow of DPPC on water. We discovered that by cross correlating consecutive BAM images, the velocity field could be obtained even in cases where no co-existing phase domains were present. Velocimetry by cross correlating BAM images of single phase (liquid or solid) flowing monolayers, with their unresolved fine grain structure, is akin to laser speckle velocimetry, where overlapping images of particles in the image plane interfere
FIG. 2. Measured equation of state for DPPC on pure water\textsuperscript{27} in terms of surface pressure (reduction in the surface tension from that of a clean surface, about 72.3 dyne/cm at 22 °C) and area coverage. The BAM images, obtained at 45 × magnification using an objective with NA = 0.28 (resolving power of 1.1 μm), show co-existing LE/LC phase domains in the intermediate range of monolayer concentration.

due to scattering of coherent light and distinct particles are not identifiable. Our utilization of PIV is also analogous to the velocimetry in Ref. 25 where infrared images were cross correlated to determine the velocity field. The Brewster angle microscope used in the present study utilized an Nd:YAG laser with 5 ns pulse (532 nm), see Ref. 26 for additional details.

The equation of state for DPPC, shown in Fig. 2, was measured using the standard technique of compression in a Langmuir trough, detailed in Ref. 28. The surface pressure, i.e., the reduction in the surface tension from that of a clean surface due to the presence of the monolayer, is plotted against the area per molecule. Included in the figure are BAM images of DPPC monolayers at various surface concentrations on water. Co-existing liquid expanded/liquid condensed (LE/LC) domains can be readily identified at intermediate surface concentrations. Figure 3 compares our measured equation of state with others reported in the literature. All of them were reported for DPPC alone on pure water at room temperature (20–23 °C). Subtle differences, for example, in material purity and water pH makes it difficult (if not impossible) for the isotherms from different studies to match exactly. Despite the variations, they generally show a similar phase behavior. The comparison between the present measurements and published data shows the best agreement with Ref. 1.

Although no distinct features are discernable at area coverage greater than about 0.8 nm\textsuperscript{2}/molecule (small surface concentrations) and less than about 0.6 nm\textsuperscript{2}/molecule (large surface concentrations), the displacement field of the monolayer can be obtained by the common technique of digital particle image velocimetry (DPIV)\textsuperscript{29} applied to BAM images. DPIV (or simply PIV) involves cross correlating sampling windows between sequentially obtained images, in which the resolution can be improved with progressively smaller sampling windows.\textsuperscript{30} Many flow studies have already utilized BAM, but they involve tracking of specific features.\textsuperscript{6,31–34} Cross correlating BAM images of monolayers with a single phase, i.e., without co-existing (LE/LC) phase domains such as the middle-two images in Fig. 2, have not been published before, to our knowledge. A key feature of the present BAM system is the fast pulse laser, which produces unsmeared images. For the measurements presented here, an open source PIV software\textsuperscript{35} was utilized to cross correlate the BAM images.
FIG. 3. Comparison between our measured equation of state (shown in Fig. 2) with data from the literature.

The consistency and accuracy of the interfacial azimuthal velocity profile $v_s(r)$, scaled by $\Omega r_o$, obtained via cross correlated BAM images can be assessed in Fig. 4. The BAM data is compared to the profile obtained using 50 $\mu$m Teflon particles tracked on the surface, both for the same monolayer and flow conditions. Common problems in using particles to measure interfacial velocity, such as those due to uneven spreading of particles on the surface, particle agglomeration, variability in wetting, and the resulting errors due to particle submersion depth, produce significant noise in the data. On the other hand, velocity measurements obtained by cross correlating BAM images is non-invasive, much less noisy, and consistent with numerical predictions, described below.

FIG. 4. Non-dimensionalized surface azimuthal velocity profile as measured in our apparatus using conventional particle tracking and cross correlated BAM images for $Re = \Omega^2 \pi^2 / \nu = 600$ and $\Pi = 5$ dyne/cm. For all BAM measurements presented here and in Figs. 5 and 6, the magnification was $7\times$ with resolving power of 3 $\mu$m.
III. RESULTS AND DISCUSSION

The interfacial azimuthal velocity profiles for various monolayer surface pressures and floor rotation rates are presented in Figs. 5 and 6 for Reynolds numbers of 100 and 600, respectively. The computed profiles in these figures were determined using the Navier-Stokes equations for the bulk flow with the boundary conditions at the monolayer-covered free surface provided by the Boussinesq-Scriven surface model,\textsuperscript{18, 36, 37} our technique is described in detail in Ref. 38. The flow is governed by the rotation rate of the bottom, given in non-dimensional form as the Reynolds number, $Re = \Omega r_0^2 / \nu$, which is a ratio of the viscous time to the rotation period, and by the ratio of the depth of the water to the annular gap. In general, one would need to take into account surface tension gradients due to monolayer interfacial gradients, but when the surface is completely covered and the secondary meridional flow in the bulk is relatively weak, the flow on the interface is radially stagnant and the monolayer only flows in the azimuthal direction.\textsuperscript{20} Then the tangential stress balance at the interface reduces to

$$
\frac{\mu}{\mu r_0} \frac{\partial v}{\partial z} \bigg|_{z=h} = \mu^t \left( \frac{\partial^2 v^t}{\partial r^2} + \frac{1}{r} \frac{\partial v^t}{\partial r} - \frac{v^t}{r^2} \right),
$$

where $v$ (cm/s) is the azimuthal velocity, the surface azimuthal velocity is $v^t(r) = v(r, z = h)$, $r$ and $z$ (cm) are the radial and axial directions, $\mu$ [g/(cm s); Poise] is the shear viscosity of the bulk, and...
\( \mu^s \) (g/s; surface Poise) is the surface shear viscosity. Now the only interfacial variable in the system is the surface shear viscosity. This is also true in the inertialless limit, \( Re \rightarrow 0 \). With finite \( Re \), the essential difference is that the inertia of the system redistributes the vortex lines and so the \( v \)-profile at the interface requires the solution of the Navier-Stokes equations. However, as in the inertialless limit, we only need to measure the azimuthal velocity at the interface to determine \( \mu^s \) (by matching the measured velocity profile to the computed profile at the appropriate \( \mu^s \)).

Our measurements at the largest inertia used (\( Re = 600 \)) show that the average radial velocity at the interface is about \( 3 \times 10^{-4} \) cm/s, or \( \sim 5 \times 10^{-4} \) \( \Omega r_0 \), over the range of surface pressures considered; this is three orders of magnitude smaller than the corresponding azimuthal velocity and is at the experimental noise level. The absence of radial velocity is expected for any insoluble monolayer at area coverages corresponding to measurable surface pressures. This provides experimental justification in utilizing the radially stagnant flow approximation in the computations.

The radial profiles of the azimuthal velocity at the interface, presented in Figs. 5 and 6, show that at low surface pressures (\( \Pi \lesssim 10 \) dyne/cm), the monolayer exhibits a viscous and Newtonian behavior. The flow is Newtonian since the measured profiles fit the predicted profiles and are independent of the Reynolds number (covering a wide range of shear rates). At the lowest surface pressure presented, \( \Pi = 5 \) dyne/cm, the surface shear viscosity is less than about \( 10^{-3} \) g/s. At large concentrations of the monolayer (area per molecule less than about 0.5 nm\(^2\)) with surface pressure \( \Pi \gtrsim 15 \) dyne/cm, there is a clear departure from Newtonian behavior. First, the monolayer exhibits Reynolds number dependence. At \( \Pi = 15 \) dyne/cm, the monolayer appears to follow the
predicted shape of the velocity profile, but depending on the Reynolds number different values of surface shear viscosity are exhibited. At the largest concentration, the monolayer velocity profile is not only Reynolds number dependent, but also has a somewhat flatter shape than expected (see Fig. 5(e)), suggesting shear thinning. Shear thinning behavior can also be deduced from the fact that at the lower Re, the surface shear viscosity is apparently larger than at larger values of Re.

It should be emphasized that the shape of the velocity profile at the interface is dependent on the flow regime as well as the bulk flow geometry. For example, Ref. 20 showed experimentally and numerically that aside from the surface shear viscosity of the monolayer, the shape of the velocity profile on the surface of the deep-channel viscometer depends strongly on the flow inertia. On the other hand, in a different flow system, where the monolayer is driven by the action of surface pressure through a long narrow slit, Ref. 40 found surface velocity profiles that were much flatter. In general, the surface velocity is inherently coupled to the bulk flow.

The surface shear viscosity for the two values of Re over a range of surface pressures deduced from Figs. 5 and 6 are summarized in Fig. 7. The figure shows that at the lowest surface pressure, the monolayer exhibits a relatively small surface shear viscosity, consistent with more liquid phases (LE and LE/LC). With increasing monolayer packing and corresponding surface pressure, the viscosity increases and exhibits a clearly non-Newtonian behavior at $\Pi \gtrsim 15$ dyne/cm where condensed phases are observed (LC or solid). The shear thinning behavior continues with increasing surface pressure and the disparity between the surface viscosity deduced from the two floor rotation rates increases further at the highest surface pressure measured ($\Pi = 35$ dyne/cm), where the monolayer appears to exist as a solid phase.

For comparison, Sacchetti et al. 39 report measurements of $\mu_s$ using a canal surface viscometer, where the monolayer is driven by a surface pressure gradient along a relatively long slit. Their study focused on DPPC at relatively large surface pressures, with $\Pi$ between about 22 dyne/cm and 43 dyne/cm. At their lowest surface pressure, their measured $\mu_s$ is about 30% of our measurement at the larger floor rotation rates ($Re = 600$); see Fig. 7. At $\Pi = 35$ dyne/cm, their measurements are very close to our data at the larger floor rotation rate. Measurements reported by Ding et al. 9 obtained using a magnetic needle surface shear viscometer are also presented in Fig. 7. For these comparisons, we have averaged the surface shear viscosities that they reported at 20 °C and 25 °C. At the lowest surface pressure ($\Pi = 5$ dyne/cm), they report a surface shear viscosity that is about twice our measurements. At an intermediate surface pressure between $\Pi = 10$ and 15 dyne/cm, their measurements are in agreement with ours. At larger surface pressures, the measurements of Ding et al. 9 diverge from ours, indicating much larger surface shear viscosity. The bifurcation delineating Newtonian and non-Newtonian flow that we have demonstrated for monolayers with surface pressures above 10 dyne/cm appears to piece together the seemingly desperate results obtained by others, namely the very low shear rate exerted by a magnetic needle 9 and the relatively large shear rates exerted on the monolayer flowing along a slit. 39
It should be noted that at surface pressures greater than or equal to about 42 dyne/cm, we find that the monolayer ceases to flow on the surface of the channel. Our technique, which relies on steady-state surface velocity measurements, cannot be used to quantify the surface shear viscosity under such circumstances. This limit is shown schematically as asymptotes extending our measurements in Fig. 7, indicating that the surface shear viscosity becomes unbounded based on our technique. Other methods have been used to study these regimes. For example, Ref. 41 reports finite shear modulus and frictional shear losses of DPPC monolayers at such solid (“gel”) states.

Even though the range of Reynolds number utilized, \( Re \in [100, 600] \), is large compared to unity, shear rates exerted on the monolayer in our apparatus are modest. Specifically, for \( Re = 100 \), the surface shear rates vary between zero and a maximum of about 0.06 s\(^{-1}\), while for \( Re = 600 \) they vary between zero and about 0.4 s\(^{-1}\). In the context of pulmonary flows, these ranges of values cover the shear rates experienced during surfactant infusion in the vast majority of networks of branches and alveoli.42

IV. CONCLUDING REMARKS

The range of states where the most widely studied phospholipid monolayer (DPPC) exhibits Newtonian behavior and its transition to nonlinear response were presented here. This was achieved by a novel analysis of Brewster angle microscopy images, which works solely by the reflectivity of the monolayer without any dyes or other additives, and the results were interpreted using computations based on the fully-coupled hydrodynamic equations. The significance of the new interfacial velocimetry technique is that it can be applied over a wide range of monolayer packing and phase behavior. The technique is also significant because of its optical nature, since it can be applied over a wide range of length scales and thus used to non-invasively study the rheology of monolayer micro-structures.

Finally, it should be noted that DPPC films are often reported to be viscoelastic,43 so that a surface shear viscosity alone would not be sufficient to fully describe the interfacial rheology. The results of the present study have identified a range of surface pressures where DPPC does behave as a Newtonian film when subjected to shear. This is perhaps due to the film responding to a relatively high shear rate. Further improvements in our understanding and modeling of surface shear viscosity are needed, not only for shearing flows but also in flows that involve planar dilation or compression of the monolayer. This is because the sum of the surface shear and surface dilatational viscosities appears in the tangential stress balance.\(^{18,36,37}\) The situation with surface dilatational viscosity is even more complicated and anomalous behavior has been widely reported for surface dilatational viscosity.\(^{26,44}\) This is in part due to the effects of surface tension gradients (source of Marangoni stress) being coupled to the effects of dilatational viscosity,\(^{18}\) as well as the coupling with the surface shear viscosity.

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