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Single-particle Brownian dynamics for characterizing the rheology of fluid Langmuir monolayers

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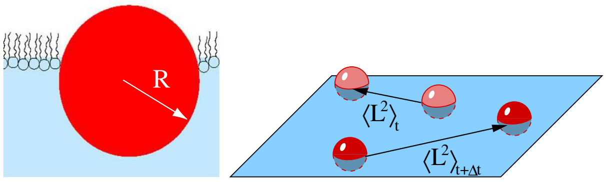
Abstract – The Brownian movement of a submicron diameter sphere has been used to study the rheology of Langmuir monolayers of short-chain surfactants in the low-density limit (liquid-expanded phase). We show how the shear viscosity can be derived from previously measured diffusion coefficients (Sickert M. and Rondelez F., *Phys. Rev. Lett.* **90** (2003) 126104) by using recent theoretical models for a sphere of size much larger than the monolayer thickness. We report the surface viscosity as a function of the occupied surface fraction, which we believe are the first such estimates based on physically consistent experiments and theory. The two models yield values of the surface viscosity 1–5 $\times 10^{-10}$ Ns/m and 2–8 $\times 10^{-10}$ Ns/m over the entire range of surface densities of the liquid-expanded phase.

Introduction. – Proteins, lipids, phase-separated domains, and other membrane-bound objects diffuse in the plane of an interface. Such diffusion can be important to transport pathways in biological systems. Conversely, measurements of the diffusion of colloidal particles can yield information on the rheology of the interface. A practical route for the rheological characterization of Langmuir monolayers of amphiphilic molecules spread at the air-water interface was introduced by Sickert and Rondelez [1], who tracked the motion of submicron-sized spherical particles that were placed in the surface film. This approach is similar in spirit to the single-particle and multiple-particle tracking methods introduced to study the rheology of three-dimensional materials [2].

The original model of Saffman and Delbrück [3,4] describes Brownian motion in lipid membranes by considering the diffusing object as a circular disk that spans the membrane. In reality, since the film is molecularly thin (the length of a typical surfactant is a few nanometers), many naturally occurring membrane-bound objects, or objects placed in the membrane to measure the membrane properties, are substantially immersed in the surrounding liquid. The case of a sphere that protrudes into the subphase has been dealt with in several theoretical papers. In an important paper, Danov *et al.* [5] studied numerically the motion of such a sphere with various immersion depths in a membrane characterized by surface shear and dilatational viscosities. However, the surface pressure was treated as constant, and therefore the results only apply to compressible surface films. This feature is a severe limitation in the case of Langmuir monolayers that must be considered as incompressible, even in their dilute liquid-expanded state. The reason for this incompressibility is the same as the explanation for the incompressible flow of gases when the velocity of the moving object is much lower that the speed of sound [6]. This point was demonstrated experimentally by Barentin *et al.* [7] for monolayers made of short chain, as well as polymeric, surfactants. Subsequent theoretical work [8] has accounted for membrane incompressibility by using a linear equation of state for the surface pressure as a function of the surface concentration, but the coupling with the subphase liquid was neglected. For one reason or another, therefore, none of the above approaches was appropriate to extract values of the surface viscosity from the diffusion experiments reported by Sickert and Rondelez [1,9,10].

A proper model model to extract values of the surface viscosity from the Brownian motion of floating particles has to account for the protrusion of the sphere into the subphase on the one hand, and for the incompressibility of the viscous monolayer, on the other hand. In this paper, we present two recent theories, by Fischer *et al.* [11] and



(a) (b)

Fig. 1: (a) A particle of radius R is partially immersed in the monolayer and subphase. (b) The surface diffusivity is determined by measuring the average change in separation distance of particle pairs which is an approach that eliminates small drifts present in the experiment.

Stone [12], that incorporate these two requirements and we discuss their range of applicability in terms of surface viscosities and depths of immersion. We then select the model that corresponds best to the experiments described in [1], in particular considering the value of the contact angle between the particle and the water surface. As a representative example, we extract values of the surface viscosity for a surfactant monolayer of N-palmitoyl-6-n-penicillanic acid (PPA) in the liquid-expanded phase. In this case, there is a significant dependence of the measured diffusion coefficient D on the surface density and we are thus able to provide surface viscosities values as a function of surface concentration. In two other cases, namely pentadecanoic acid and L-α-dipalmitoylphosphatidylcholine, the diffusion coefficient is independent of the surface density, which means that the monolayer viscosity is smaller than our detection limit. Most significantly, we show that, even in this viscosity limit, the ratio of the measured diffusivity D, relative to the value measured in the absence of surfactant, D_0, is $D/D_0 = 0.8$. This result is consistent with the expectation for incompressible, inviscid monolayers. These data obtained on three different surfactants, and the basic approach, highlight the potential usefulness of this method of Brownian particle rheology for characterizing fluid membranes.

Experiments. – The experimental set-up has already been described elsewhere [1] and we only give a sketch of the basic principle of the experiments. We optically observe the Brownian motion of $0.4\,\mu$m diameter latex particles that have been deposited on the monolayer (see fig. 1a). The monolayer is contained in a temperature-controlled Langmuir trough mounted on an inverted microscope. Care is taken to avoid air currents and thermal convection. In order to reduce the influence of macroscopic drift currents, we do not observe the absolute position of the beads as a function of time. Rather, we group all particles in pairs and we measure their relative separation $\langle L^2 \rangle$ (see fig. 1b). If the motion is random and isotropic one expects the squared separation distance to increase linearly with time. The slope gives the surface diffusion coefficient D that is converted to a surface viscosity by using an appropriate hydrodynamic theory.

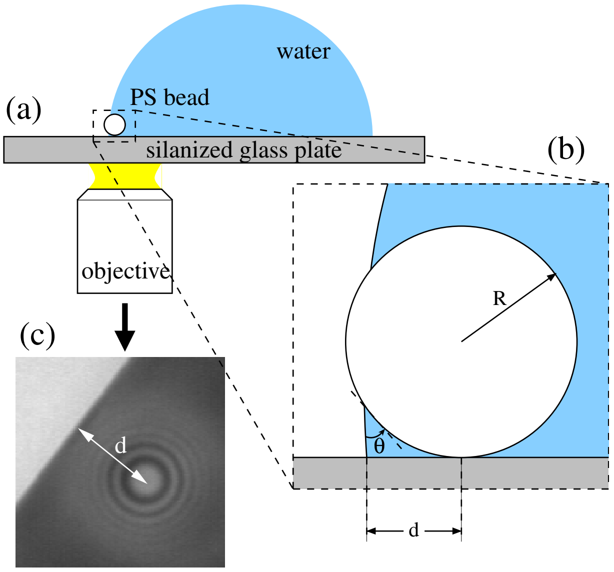


Fig. 2: Experimental determination of the contact angle for the latex particles in water. (a) A latex particle sits on a glass slide beneath a drop of water. (b) Close-up view of the particle. (c) Interference fringes mark the center of the particle which is a distance d from the contact line.

One important parameter is the bead density, which should be low enough that each bead can be considered to move independently from all others. Typically the bead density is $1/400\,\mu\text{m}^2$. The small size of the beads also precludes significant deformations of the interface by gravity, which otherwise would cause spurious capillary interactions. The second important parameter is the depth of immersion of the particle for which we have measured the contact angle. In order to determine the particle-fluid contact angle θ, we have developed a novel method [13] that consists in forming a sessile water droplet on the surface of a glass microscope slide and depositing a dilute solution of latex particles (greater than one micron) on its surface. The beads sediment by gravity towards the glass-water contact line where they are observed with an inverted microscope.

A typical microscope image of this experimental procedure is shown in fig. 2. The water-glass contact line and an interference pattern of the bead are visible. The center of the Newton rings marks the bead center. With the measured distance d to the water-glass contact line, which corresponds to the sphere's penetration depth, and denoting the water-glass contact angle by β, we calculate the contact angle θ using the expression $\theta = \pi/2 - \arcsin\left(\cos\beta + \frac{d}{R}\sin\beta\right)$. For a clean water surface, the contact angle is $50 \pm 5°$. Consequently, the bead is more than half-immersed in the subphase. Also, a surfactant monolayer can be formed by bringing a droplet of an amphiphile-spreading solution in contact with the sessile water drop prior to bead deposition. For a saturated monolayer, the typical contact angle is $30 \pm 5°$ (as measured for PDA). We have not attempted to vary the surface density experimentally. Application of Young's law allows a fair estimation of the contact angle for any surface density, provided the interfacial tension γ has been measured separately (here it is known from independent surface pressure isotherms measurements), *i.e.* $\cos\theta = (\gamma_0/\gamma)\cos\theta_0$. Since the highest surface pressure $\gamma_0 - \gamma$ attained in our experiments is $10\,\mathrm{mM/m}$, then changes in θ are at the most from 50° to 46°. Therefore, we have neglected this small variation in contact angle in our data analysis.

Phase diagrams of the surfactants. – Monomolecular films of three different amphiphiles were spread from chloroform solutions on the surface of the Langmuir trough: pentadecanoic acid (PDA), *L*-α-dipalmitoyl-phosphatidylcholine (DPPC) and *N*-palmitoyl-6-*n*-penicillanic acid (PPA). The monolayer surface pressure was measured, using a microbalance, as a function of the average area per molecule by the Wilhelmy plate method. The results are shown in fig. 3a and allow us to infer the phase diagram and some properties of the surfactants.

At a large area per molecule, A, the surface pressure is low and the monolayer is in the liquid-expanded state (also called L1). As the area per molecule is decreased, a kink is observed in the surface pressure isotherm, which indicates the onset of a new liquid phase, called liquid condensed or L2. Independent epifluorescence microscopy shows that the transition is first order: domains of L2 phase coexist with a continuous L1 phase. In this two-phase region, the monolayer is essentially incompressible and the surface pressure variations are small.

The sudden increase in pressure at low area per molecule marks the complete transformation of the monolayer into the L2 phase in which the molecules are close-packed. The molecular cross-section, A_0, can then be estimated. We have followed the standard protocol for extracting A_0 from the surface pressure isotherms, *e.g.*, [14]. More specifically, we take the tangent to the curve at the maximum surface pressure measured experimentally and A_0 is the intercept where this tangent extrapolates to zero pressure. We find, respectively, $A_0 = 19\,\text{Å}^2$, $38\,\text{Å}^2$ and $42\,\text{Å}^2$, consistent with the geometrical cross sections determined for single-chain PDA, double-chain DPPC, and single-chain but bulky head-group PPA. Slightly different values are sometimes reported in the literature, but small variations do not affect our general conclusions.

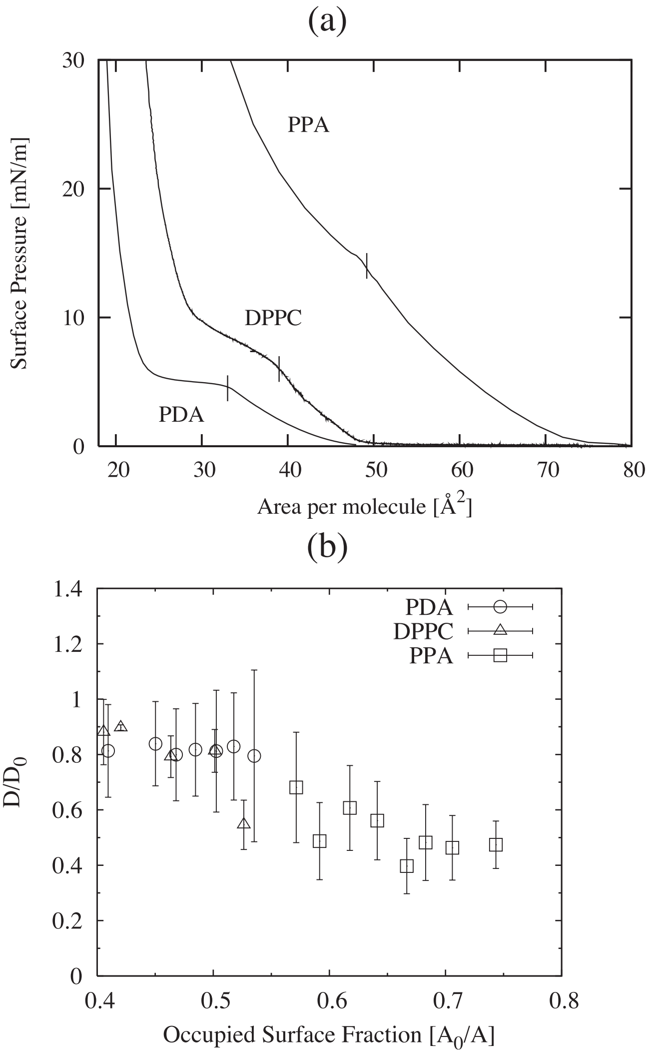


Fig. 3: (a) Measured surface pressure *vs.* the surface concentration, which is reported as surface area per molecule: isotherms of pentadecanoic acid (PDA), *L*-α-dipalmitoyl-phosphatidylcholine (DPPC) and *N*-palmitoyl-6-*n*-penicillanic acid (PPA), all obtained with an aqueous phase with $p\mathrm{H} = 2$. Note that the DPPC isotherm has been shifted towards smaller areas by dividing its area values by a factor of two. This accounts for the bicaudal nature of this molecule. The isotherms have been recorded at 22 °C. The vertical solid lines indicate the end of the liquid-expanded phase. (b) Measured diffusion coefficients for spherical particles in monolayers of three different surfactants as a function of the occupied surface fraction A_0/A, as reported in [1]. The diffusion coefficients D are reported relative to the diffusion coefficient D_0 for a clean water interface (*i.e.* an inviscid and compressible interface).

Measurements of the diffusion coefficient as a function of the monolayer surface density. – The experiments monitoring the surface diffusion of particles have been performed exclusively in the liquid-expanded phase (L1). Since this phase is homogeneous and isotropic [15,16] the shear viscosity is simply connected to the diffusion coefficient of the probe particle. The diffusion data for the three surfactants, as taken from Sickert and Rondelez [1], are shown in fig. 3b as a function of the occupied surface fraction, A_0/A. It should be noted that the diffusion coefficients D are expressed relative to the diffusion coefficient D_0 for a clean water interface (*i.e.* an inviscid and compressible interface). In our experiments $D_0 = 1.26 \pm 0.19\,\mu\mathrm{m}^2\mathrm{s}^{-1}$. This procedure is useful in order to minimize the influence of systematic artifacts such as long-range hydrodynamic interactions[1] between the probe particles, which are expected to be of the same magnitude in both situations. We also note that our experiments cover a limited range of A_0/A, typically between 0.45 and 0.75. The lower limit is imposed by our detection sensibility. Reaching higher A_0/A values is precluded by the onset of the L1-L2 coexistence region. In this two-phase region, the continuous L1 phase is of constant density and contains disk-like L2 domains. Therefore, the system becomes akin to a two-dimensional suspension, which is outside the scope of this paper [18].

The data in fig. 3b show a gradual decrease from $D/D_0 = 0.8$ to 0.4 as the monolayer is compressed in its liquid-expanded phase. The high range of A_0/A corresponds to PPA, whereas the low range corresponds to PDA and DPPC. Upon closer examination, we observe that most of the D/D_0 change occurs for $A_0/A > 0.5$, which is for PPA. In the case of the data for PPA we have performed a linear fit of D/D_0 *vs.* A_0/A and obtained a goodness of fit $R^2 = -0.64$ and a negative slope equal to -0.97 ± 0.48; if we remove the two most outlying data points, then for the remaining six data points we obtain a much better correlation with a goodness of fit $R^2 = -0.94$ with a negative slope of comparable value (-1.26 ± 0.2). For this compound, the diffusion coefficient varies with the occupied surface fraction and so we can seek estimates of the shear viscosities of the surfactant monolayer as a function of the surface density. This step requires a hydrodynamic theory for the motion of spheres partially immersed in the monolayer and subphase, which is described below. On the contrary, the measured diffusion coefficients are essentially independent of the occupied surface fraction for $A_0/A < 0.5$. For PDA and DPPC, the diffusion coefficient remains 25% lower than for the free water interface, which is characteristic of incompressible, but nonviscous, monolayers [7]. Conversely, since the measured D_0 for the free water surface is larger by 25% than the extrapolated D value for the very dilute monolayers, we conclude that the free interface is effectively clean, *i.e.* free of any significant amounts of contaminants. For similar data and interpretation, see fig. 5 of Barentin *et al.* [7].

Disks: Incompressibility effects for nonviscous surface films. – We first briefly describe a (nearly) two-dimensional analogue of the familiar three-dimensional Brownian motion. A particle, trapped symmetrically at the membrane, translates at speed U parallel to the interface. The motion requires a force F parallel to the interface and the coefficient of hydrodynamic resistance is $\zeta = F/U$, with the diffusion coefficient $D = k_BT/\zeta$. A model for membrane-restricted motions takes the particle to be a thin circular disk of radius R [3,19] and the dynamics are characterized by the dimensionless parameter $E = \eta_s/\eta R$, where η_s is the surface viscosity and η is the subphase viscosity.

These early studies highlighted the role of incompressibility of the surface film. For $E = \frac{\eta_s}{\eta R} \to 0$, which corresponds to a film with vanishing viscous effects, $\zeta(E \to 0) = 8\eta R$. Instead, if the disk translates at a free liquid-air interface, then $\zeta_0 = \frac{16}{3}\eta R$; from now on we use a subscript 0 to refer to experiments with such clean interfaces. Therefore, even for a film of vanishing η_s the coefficient ζ is different from that of a clean water interface, *i.e.* $\frac{\zeta(E\to 0)}{\zeta_0} = \frac{3}{2}$. The increased resistance of a surface film relative to a clean interface is a consequence of incompressibility of the film, which constrains the motions of the surrounding liquid. The fact that the film can have a low viscosity, yet still be incompressible, is due to the rapid equilibration of the monolayer [9]: the thermal relaxation time is set by the sound speed, which is the same order of magnitude ($O(10^3)$m/s) in fluid membranes as it is in ordinary liquids; density variations at the scale of ten microns should be eliminated in tens of nanoseconds.

A membrane-trapped particle —protrusion into the subphase. – Recently, the coupling of in-plane motion accounting for protrusion into the subphase to the bulk phase hydrodynamics has been treated by two groups. Stone [12] considered an ellipsoidal particle with aspect ratio $0 \leqslant \epsilon \leqslant 1$ ($\epsilon = 1$ corresponds to a sphere). For symmetry reasons the calculation required a 90° contact angle. In the limit $\epsilon \ll 1$, the theory leads to the in-plane force $F(E) = \eta RU(F^{(0)}(E) + \epsilon F^{(1)}(E) + \cdots)$, where the dimensionless coefficients $F^{(0)}$ and $F^{(1)}$ are known numerically. For the case that the sphere ($\epsilon = 1$) *translates in an unbounded fluid* this perturbation approach gives the exact solution (Stokes law) to within 5%. Assuming the same extrapolation for the problem at hand, we estimate the surface diffusivity for any E for a sphere by setting $\epsilon = 1$. For a sphere translating along a clean interface, with a 90° contact angle, the resistance coefficient is $\zeta_0 = 3\pi\eta R$. Then, for a membrane-trapped particle, we predict that the diffusion coefficient, relative to a clean interface, depends on E as

$$\frac{D}{D_0} = \frac{3\pi}{F^{(0)}(E) + F^{(1)}(E)}. \tag{1}$$

The numerical results are shown as the thin solid curve (labeled "Stone") in fig. 4, together with available numerical and analytical results for a circular disk by Stone and Ajdari [20] and Hughes *et al.* [19]. All approaches lead to the same dependence for sufficiently large E ($E > 4$), since in this large surface viscosity limit the detailed shape of the object does not matter. If $E < 1$, the differences between the sphere and the disk results, however, are very significant. In the $E \to 0$ limit, $\frac{D}{D_0} = \frac{3\pi}{F^{(0)}(E \to 0)} \approx 0.8$,

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[1] For Brownian particles in a soap film, Cheung *et al.* [17] have shown that hydrodynamic interactions can decrease the measured diffusion coefficient by as much as 30%, when the particle separation distance is 10 times their diameter. In our experiments the average separation is 30 times the particle diameter. We believe that this effect may explain why the viscosity of the water subphase from the D_0 value determined by Sickert and Rondelez [1] was 24% too large compared to literature data.

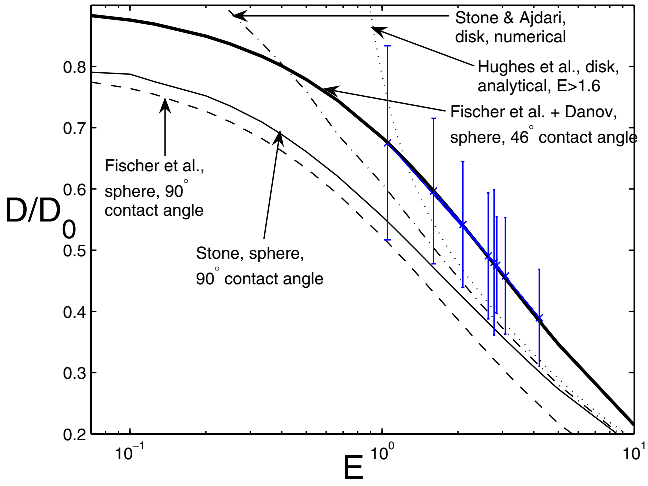

Fig. 4: The surface diffusivity, relative to the value for a clean interface, as a function of the surface viscosity parameter, $E=\eta_s/\eta R$. The theoretical predictions based on a disk have been normalized by 3π to account for the resistance of a sphere along a clean interface. Hughes *et al.* [19] determined numerically the resistance coefficient for a disk for all E. For $E>1.6$ they also developed an asymptotic approximation, $\frac{\zeta(E)}{\eta R}=\frac{4\pi E}{\left(\ln(2E)-\gamma+\frac{4}{\pi}E^{-1}-\frac{1}{2}E^{-2}\ln(2E)\right)}$, where $\gamma\approx 0.5772$ is Euler's constant. This theoretical prediction is shown in the figure (it diverges as $E\to 1$ since this is outside the range of validity of the approximation). Numerical results for a disk based on the approach of Stone and Ajdari [20] are shown also. Experimental values of D/D_0 for microspheres in a PPA monolayer have been placed on the "Fischer-Danov" theoretical curve for spheres straddling the interface. The error bars correspond to the measurement uncertainties in the diffusion coefficient.

while for disks $\frac{D}{D_0}=\frac{2}{3}$. We repeat that this model is valid for all E but assumes that the contact angle is 90°.

Fischer *et al.* [11] have taken a complementary approach of explicitly addressing the question of immersion depth (*i.e.* contact angle θ) by using a numerical method general enough for a wide class of particle shapes. However, they were only able to obtain results for $E\ll 1$. In their notation, $\zeta(\theta)=\eta R(k_T^{(0)}(\theta)+Ek_T(1)(\theta))$, where $E\ll 1$ and the coefficients $k_T^{(i)}$ are functions of contact angle that are determined numerically. Hence, again denoting the resistance of the object diffusing on a free surface by $\zeta_0(\theta_0)$, we obtain

$$\frac{D}{D_0}=\frac{\zeta_0(\theta_0)}{k_T^{(0)}(\theta)+Ek_T^{(1)}(\theta)}. \qquad (2)$$

The numerical results are also shown in fig. 4 in i) the case where $\zeta_0(\theta_0=90°)$ and $\theta=90°$ in order to compare with the model of Stone [12] and ii) $\zeta_0(\theta_0=50°)$ and $\theta=46°$ in order to compare with our experiments. The $\theta=46°$ value was calculated using Young's law, the contact angle $\theta_0=50°$ for pure water and a surface pressure of $10\,\mathrm{mN\,m^{-1}}$ for the PPA monolayer in its liquid-expanded phase (see fig. 3a). For an inviscid and compressible surface [5], $\zeta_0=3\pi$ for $\theta_0=90°$ and $\zeta_0\approx 4\pi$ for $\theta_0=50°$. Comparing the theoretical predictions in the $E\to 0$ limit, we expect $\frac{D}{D_0}=\frac{\zeta_0(50°)}{\zeta(46°,E=0)}\approx 0.84$. The values of D/D_0 in fig. 3b are in excellent agreement with this prediction.

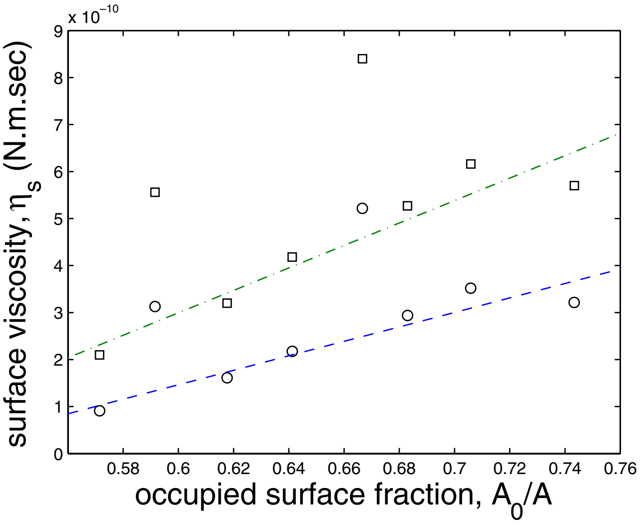

Fig. 5: Calculated surface viscosity of PPA as a function of the occupied surface fraction, plotted as A_0/A. The two sets of data are extracted from the measured diffusivities, using the Fischer-Danov (open squares) and Stone (open circles) models, respectively (see text for details). The lines are best linear fits to the data, after extracting the two outlying data points.

Surface viscosities of Langmuir monolayers. – The above finite-immersion models provide a framework for extracting the surface viscosity from the diffusion data. For each experimental measurement of D/D_0 we determine from fig. 4a value of the dimensionless parameter $E=\eta_s/\eta R$ for each surface fraction. Once E is known, η_s is obtained. Obviously, the model that appears best suited to our experiments is a "modified Fischer-Danov" model: we use the value $\zeta_0=4\pi$ determined by Danov *et al.* [5] for the resistance coefficient of a sphere at a clean, compressible surface and with a contact angle $\theta_0=50°$ and the prediction of Fischer *et al.* [11] for ζ for a sphere in a surfactant-covered interface with $\theta=46°$. The eight experimental data points are placed on the theoretical curve in fig. 4, which yields eight values of the surface viscosity that are plotted *vs.* occupied surface fraction as the squares in fig. 5. The uncertainty in the diffusion coefficient introduces significant uncertainty in the determination of E and consequently on the surface viscosities as evidenced in fig. 4.

Since this use of the results of Fischer *et al.* [11] is only valid for $E\ll 1$ and as our D/D_0 values correspond to $1<E<4$, we cannot claim that the best values for the surface viscosity have been determined. Fortunately, the model of Stone [12], which should be reasonable for all E, but for a contact angle of 90°, provides a lower bound for the E. The viscosity data so determined are shown for comparison with circles in fig. 5. We observe that the two estimates of η_s differ by about a factor of two. We find $2\times10^{-10} < \eta_s < 8\times10^{-10}$ Ns/m in the first case and $1\times10^{-10} < \eta_s < 5\times10^{-10}$ Ns/m in the second case. These values are 2–3 times higher than our previous estimate [10]. Indeed, the viscosity values had been tentatively estimated using the master curves between D and E established using the results of Danov *et al.* [5] and Hughes *et al.* [19], respectively. However we knew that neither of these two theories could be straightforwardly applied to the experimental situation. Thus, we conclude here that the actual surface viscosity lies somewhere between the two lines (best fits to the data after removing the two outlying data points) in fig. 5. We remark that we can also estimate an upper bound for the surface viscosity of DPPC and PDA. Since these surfactants have $D/D_0 \approx 0.8$ for an occupied surface fraction $A_0/A = 0.5$, then with the results in figs. 4 and 5 we calculate an upper limit $\eta_s < 1\times10^{-10}$ Ns/m; the data at the lowest surface fractions may have surface viscosities ten times smaller. Finally, we want to re-emphasize that the D/D_0 values for low A_0/A do not extrapolate to unity, but to a significantly smaller value of about 0.85. This result is in excellent agreement with the Fischer-Danov model that predicts a value of 0.84 and also confirms the observations of Barentin *et al.* [7]. The feature that $D/D_0 \neq 1$ provides an example of the apparent paradox that an indetectably small amount of surfactant can affect the hydrodynamics of the diffusing bead although the monolayer has no appreciable viscous effects.

The new values of η_s provide a reference set for the surface viscosity of Langmuir monolayers in the liquid-expanded phase. Earlier determinations were very approximate. For instance, Steffen *et al.* [21] could only say that the surface viscosity was lower than 10^{-9} Ns/m for methyl-octadecanoate. Similarly, experiments on stearic acid monolayers by Barentin *et al.* [7] were limited by the 10^{-7} Ns/m sensitivity limit of their apparatus. Using optical techniques, Schwartz *et al.* [22] and Klinger and McConnell [23] could also not measure the viscosity of the liquid-expanded phase even though they were working at the onset of the L1-L2 phase transition, which is the highest possible density for the liquid-expanded phase.

To conclude, the determination of the shear viscosity in the liquid-expanded phase of Langmuir monolayers turns out to be very challenging, both experimentally and theoretically. The surface viscosities are much below the sensitivity range of most macroscopic techniques and it is necessary to use smaller-scale experiments like the Brownian diffusion method described in [1]. This approach in turn requires a delicate theoretical description due to the protrusion of the probe particle into the subphase and the hydrodynamic coupling of the two phases. The methodology described in this paper shows that reliable values of the surface viscosity can nevertheless be obtained, which highlights the potential usefulness of this method of Brownian particle rheology for characterizing fluid membranes.

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