Comment on "Shear Viscosity of Langmuir Monolayers in the Low-Density Limit"

In a recent Letter [1] Sickert and Rondelez measure the diffusion constant D of latex beads of radius R immersed into the L_1 phase of a monolayer, which they then convert into a friction coefficient $f = kT/\pi\eta RD$, where k is Boltzmann's constant, T the temperature, and η the renormalized viscosity of water. Using numerical simulations of Danov $et\ al.$ [2] they then convert the friction coefficient into a surface shear viscosity η_s. We show, that the major component of decrease measured in the diffusion constant of latex beads in monolayers as compared to the free air water surface arises from the incompressibility of the surface, not from surface shear viscous damping and that therefore their data cannot be used to extract values for the surface shear viscosity.

Typical values of f found experimentally by Sickert and Rondelez are around $f \approx 5$. A half-immersed sphere on a free compressible surface has a friction coefficient of $f = 3$. The experimental value obtained is thus 60% higher than that on a free surface.

Spreading a monolayer on top of the water surface has the following effect: Marangoni forces strongly suppress any motion at the surface that compresses or expands the surface, due to the strong dependency of surface pressure on the surfactant surface concentration. The solution of the sphere immersed into a free surface has a compressible flow. The surface is compressed in front of the bead and expanded at the rear. In the presence of surfactant this flow is no longer possible and without any surface viscous effects the friction is increased in order to rearrange the flow at the surface to an incompressible flow. For a disk immersed into the surface both the drag onto the disk on a free $f = 16/3\pi$ [3] and on an incompressible $f = 8/\pi$ [4] nonviscous surface has been calculated analytically. The increase in drag on a disk is 50% similar to that observed by Sickert and Rondelez. The formulas [2] used in the paper of Sickert and Rondelez neglect this effect by setting the surface tension to be a constant independent of the density of surfactants. Consequently Danov $et\ al.$ [2] find the free surface drag $f = 3$ in the limit of $\eta_s/\eta R = 0$. That the drag on a disk in a monolayer is that of an incompressible not that of a compressible surface has been checked experimentally [5–7]. This shows that Danovs formulas give the wrong answer in the limit of low surface viscosities. We have numerically solved the problem of a sphere with contact angle θ moving in an incompressible surface of negligible surface viscosity [8]. We find that the formula

$$f \approx \frac{16}{\pi}\cos\frac{\theta}{2} \qquad (1)$$

describes the numerical data reasonably well (accuracy better than 3%). In the limit $\theta \to \pi$ Eq. (1) coincides with the result for a disk of the radius $a = R\sin\theta$ of the three phase contact line. Using Eq. (1), the renormalized viscosity of water $\eta(22°C) = 1.24 \times 10^{-3}\ \mathrm{N\,s\,m^{-2}}$ used in Ref. [1] and a contact angle of 50°, we predict a diffusion constant of 0.98 $\mu\mathrm{m}^2\,\mathrm{s}^{-1}$. This explains the entire data for pentadecanoic acid (PDA) and the data of L-α-dipalmitoylphosphatidylcholine (DPPC) above $A > 75$ Å^2 without any surface shear viscosity. The diffusion coefficient of N-palmitoyl-6-n–penicillanic acid (PPA), however, is too low to be explained without surface shear viscosity. The proper formula to convert the diffusion constant into a surface shear viscosity, however, will be different from the theory in [2], such that the proper values of the surface shear viscosity of PPA might be 1 or 2 orders of magnitude lower than the values published in [1]. Note that due to electrocapillary effects [9] the apparent contact angle θ depends on the bead size and monolayer density. It is possible that the variation of the PPA data with the monolayer density originates from contact angle, instead of from surface shear viscosity variations.

In conclusion, we have shown that Danov's relation between drag and surface shear viscosity does not apply to this case and that the major component of decrease measured by Sickert and Rondelez in the diffusion constant of latex beads in monolayers as compared to the free air water surface arises from the incompressibility of the surface, not from surface shear viscous damping. An extraction of the surface shear viscosity from the measurements is not possible.

Thomas M. Fischer
  Department of Chemistry and Biochemistry
  The Florida State University
  Tallahassee, Florida 32306-4390, USA

[1] M. Sickert and F. Rondelez, Phys. Rev. Lett. **90**, 126104 (2003).

[2] K. Danov, R. Aust, F. Durst, and U. Lange, J. Colloid Interface Sci. **175**, 36 (1995).

[3] Sir H. Lamb, *Hydrodynamics* (Cambridge University Press, Cambridge, United Kingdom, 1932), 6th ed., Chap. 11, p. 604f.

[4] B. Hughes, B. Pailthorpe, and L. White, J. Fluid Mech. **110**, 349 (1981).

[5] J. Klingler and H. McConnell, J. Phys. Chem. **97**, 6096 (1993).

[6] P. Steffen, P. Heinig, S. Wurlitzer, Z. Khattari, and Th. M. Fischer, J. Chem. Phys. **115**, 994 (2001).

[7] S. Wurlitzer, H. Schmiedel, and Th. M. Fischer, Langmuir **18**, 4393 (2002).

[8] P Heinig and Th. M. Fischer, "The Drag on a Sphere Moving in a Monolayer of Low Viscosity" (to be published).

[9] M. G. Nikolaides, A. R. Bausch, M. F. Hsu, A. D. Dinsmore, M. P. Brenner, and D. A. Weitz, Nature (London) **420**, 299 (2002).