Lawrence Berkeley National Laboratory

Recent Work

Title

LASER-RIPPLON SCATTERING FROM LECITHIN MONOLAYERS AT THE AIR-WATER INTERFACE

Permalink

<https://escholarship.org/uc/item/8pg1x5v4>

Author

Birecki, Henryke

Publication Date

1978-06-01

RECEIVED
LAWRENCE
BERKELEY LABORATORY

NOV 17 1978

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782

Energy and Environment Division

Laser-Ripplon Scattering From
Lecithin Monolayers At The Air-Water
Interface

Henryk Birecki and Nabil M. Amer

June 1978

Lawrence Berkeley Laboratory University of California/Berkeley

Prepared for the U.S. Department of Energy under Contract No. W-7405-ENG-48

LBL-8329
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Laser-Ripplon Scattering from Lecithin
Monolayers at the Air-Water Interface

Henryk Birecki and Nabil M. Amer

Applied Laser Spectroscopy Group
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

We have measured the frequency and damping coefficient of the spontaneous, thermally excited ripplons on monolayers of L- α -dipamitoyl phosphatidyl choline at the air-water interface. The dependence of the monolayer phases on temperature and surface coverage is presented and the ripplon damping mechanisms are discussed.

1. Introduction

The unique physical properties of insoluble monolayers make them useful in many technological applications. For example, they have been employed recently in the environmental technologies of water purification and recycling of rare organic substances.

A novel application related to energy production has been proposed recently by one of us (N.M.A.). It entails the use of lyotropic liquid-crystalline monolayers for the efficient extraction of oil from oil shale deposits. This new approach requires a better understanding of the properties of these systems.

The conventional techniques for investigating insoluble monolayers include the Langmuir-Adam and the Wilhelmy balance methods (1) where static surface pressure is measured as a function of the surface area per molecule. Dynamic properties such as dilatation viscosity (dynamic surface tension) and surface viscosity are typically deduced from flow through slit studies, damping of oscillations of concentric cylinders, and damping of macroscopic surface waves (1,2). The results of these experiments are difficult to interpret because of the rather gross perturbations used to probe the experimental system.

Our experimental approach was to probe the spontaneous, thermally excited surface waves, the so called ripplons, by light scattering. (3) The strength of this technique is that both static and dynamic properties of the monolayer can be elucidated in a reliable fashion and with minimum perturbation.

In the present work we are mostly concerned with the mechanisms of ripplon damping, and with the dependence of the monolayer phase transitions on temperature and surface coverage.

2. Experimental Method

Our experimental arrangement is shown in Fig. 1. A beam, 2 mm in diameter, from an Ar⁺ laser (4880Å) or a He-Ne laser (6328Å) probed the air-water interface from the water side. To maximize the signal, the angle of incidence was slightly greater than the angle for total internal reflection. (4) Reflected light was then collected with a 30 cm focal length lens and the scattering wave vector was selected by a pinhole in the focal plane of the lens moving perpendicularly to the plane of the drawing. Light passing through the pinhole was collected on the photocathode of an FW 130 photomultiplier tube and the resulting photocurrent, after pulse shaping and amplification, was analyzed with a 4-bit real time digital correlator. Stray light scattered elastically by windows and other optical components served as the local oscillator. Instrumental linewidth was determined from measurements on pure water and comparing the results with existing theories (5,6).

Since ripplons on surfaces form dynamic gratings which phase modulate the reflected beam (7,8), the scattered light will then be frequency shifted by an amount equal to the ripplon frequency. Due to the small amplitude of the ripplons (few angstroms), light is scattered effectively only in the grating's first order, thus allowing for the investigation of one q- vector at a time.

L- α -dipalmitoyl phosphatidyl choline (DPPC) was obtained from Sigma Chemical Co. ($\geq 98\%$ purity) and was used without further purification. The monolayers were deposited on the interface by spreading from a 9:1 hexane:ethanol solution (reagent grade). Demineralized distilled water was used for the experiments. The pH was 5.2 ± 0.2 and the sample

temperature was stable to better than 0.1°C. The air over the interface was routinely purged with nitrogen to minimize DPPC oxidation.

3. Theory

We have extended the hydrodynamic theory of ripplons (5,6,9) to insoluble surfactants at interfaces. We take into account the following monolayer parameters: the static surface tension $\pi(c)$ as a function of surface coverage c ; the dilatational viscosity $\beta(c)$ which takes into account the change in surface tension due to the rate of surface change (1); the intrinsic surface viscosity $\eta_s(c)$; and the slip friction coefficient $\mu(c)$ which accounts for the difference in the velocity of the lipid film and the water (10). We assume the interface to be in the x-y plane and no motion in the y direction.

The following set of equations then describe an insoluble monolayer:

1. $\nabla \cdot \vec{v} = 0$ (water incompressibility)
2. $\rho \partial_t \vec{v} = -\nabla p + \eta \Delta \vec{v}$ (Navier-Stokes equation of motion for water)
3. $c \partial_t v_L = \frac{\partial \pi}{\partial c} \partial_x c + (\beta + 2 \eta_s) \partial_x^2 v_L - \mu (v_L - v_x (z = 0))$
(Equation of motion of the monolayer)
4. $\partial_t c + c \partial_x v_L = D \partial_x^2 c$ (Continuity equation for surface layer)
5. $v_z(t, x, z = 0) = \partial_t \xi(t, x)$ (velocity boundary condition)
6. $p(z = 0) - 2\eta \partial_z v_z(z = 0) + \pi \partial_x^2 \xi + \beta \partial_x^2 \partial_t \xi = 0$
(boundary condition on normal force acting on interface).
7. $-\eta (\partial_x v_z + \partial_z v_x)(z = 0) + \mu (v_L - v_x(z = 0)) = 0$
(boundary condition on tangential force acting on interface).

where

ξ - ripple amplitude

$\vec{v}$ - water velocity

v_L lipid velocity in the x,y plane

D molecular surface diffusion coefficient

p hydrostatic pressure

η water viscosity

ρ water density

We look for a solution of the form

$$\xi(x,t) = \xi(t) e^{iqx}.$$

Following general lines of Ref. (6), we can solve the above equation in terms of their time Laplace transforms. The result is

$$\tilde{\xi}(s) = - \frac{\xi(t=0)}{s} \left[\frac{\left(\sigma + \frac{1}{x} \frac{\xi(x)}{x+d} \right) (1 - m(x) + \theta x) + 1}{\mathcal{D}(x)} - 1 \right]$$

where

$$\begin{aligned} \mathcal{D}(x) = & [1 + (x+y)^2 - y^2 m(x) + Bx] \cdot \left[1 + \theta \left(\sigma x + \frac{\xi(x)}{x+d} \right) \right] \\ & + \left(\sigma + \frac{1}{x} \frac{\xi(x)}{x+d} \right) [(1 - m(x)) (1+Bx) - x^2 m(x)] \end{aligned}$$

$$x = s/\omega_0$$

$$\omega_0 = \sqrt{\pi q^3/\rho}$$

$$y = 2\eta q^2/\pi_0 \rho$$

$$m(x) = \sqrt{1 + 2 \frac{x}{y}}$$

$$\xi(x) = \frac{\partial \pi}{\partial c} \frac{c}{\pi} + 2 \eta_s q^3 (x+d)/\pi_0 \rho$$

$$d = Dq^2/\pi_0$$

$$B = \beta \omega_0/\pi$$

$$\sigma = cq/\rho$$

$$\theta = \rho \omega_0/\mu q$$

The power spectrum of the ripples, which is the Fourier transform of the experimentally measured correlation function is then given (6) by

$$P(\omega) = \frac{\langle |\xi(t=0)|^2 \rangle}{\pi \omega} \int_m \left\{ \frac{1}{\sqrt{1-x^2}} \left[1 + \left(\sigma + \frac{1}{x} \frac{\xi(x)}{x+d} \right) \left(1 - m(x) + \theta x \right) \right] \right\}_s = -i\omega$$

Computer calculations showed that in the range of the parameters of interest, the resulting power spectrum is very nearly Lorentzian and thus the experimental correlation data were fitted to the form

$$C(\tau) = C(0) e^{-\Gamma \tau} \cos(\omega \tau + \phi)$$

where the additional phase ϕ was needed to account for most of the deviation from Lorentzian shape.

4. Results and Discussion

Since, to a first approximation (11, 12), one expects that for a free surface $\omega = (\pi q^3/\rho)^{1/2}$ and $\Gamma = 2\eta q^2/\rho$; therefore our data (Fig. 2) are plotted as apparent surface tension $\pi = \omega^2 \rho/q^3$, and relative damping constant $g = \Gamma/2\omega q^2$. For surface coverage larger than 0.01 molecule/Å² the surface tension rapidly decreases as the number of molecules per unit area is increased until the transition region between the expanded and condensed phases of the film is reached. This is exhibited by an abrupt change in the slope of the apparent surface tension vs. coverage curve at the low coverage side, while at the high coverage end of this region the transition to the condensed phase is gradual. Further increase of surface coverage results in a rapid decrease in the surface tension. Once the full monolayer is reached addition of more molecules does not change the value of the observed surface tension.

The behavior of the damping constant is qualitatively similar to that of the apparent surface tension. It should be noted that at lower temperatures the shoulder corresponding to the expanded-condensed transition becomes much less pronounced.

No measurements are shown for coverages of less than 0.01 molecule/Å². Below that, the results were not reproducible and varied over a large range of values within a few minutes. This suggests the presence of two coexisting phases (gaseous and liquid) with average size larger than the laser beam diameter.

The theory described in Section 3 is a function of several dissipation parameters the relative importance of which can now be estimated.

We estimate the slip parameter μ to be the ratio of the water viscosity η and the mean distance between the lipid molecules; i.e., $\sim 10^5$ poise/cm. For our range of wave vectors, calculations shows that Γ was independent of μ for $\mu > 10^3$ poise/cm. Thus slip is unimportant in our case. We can also neglect the dilatational viscosity since in our range of q 's the results show no q^3 dependence for Γ which would be the case if dilatational viscosity were important.

Published values for surface viscosity of the expanded phase fall in the range of 10^{-4} and 10^{-3} surface poise, and for the condensed phase they are on the order of 1 surface poise (13, 14). From our data, we estimate the surface viscosity for the expanded phase to be $< 10^{-5}$ surface poise, otherwise the theoretical q -dependence of the damping constant will be in large disagreement with the observed values and our high damping values at low coverage could not be accounted for. The damping in the expanded phase is thus due to the particular combination of surface compressibility and surface tension.

In the condensed phase our results are consistent with the behavior of an incompressible film. However, since the compressibility values derived from our surface tension data are too large to account for an incompressible behavior, therefore we are lead to conclude that surface viscosity is an important damping mechanism in the case of the condensed phase and that it is $> 10^{-3}$ surface poise. To verify this conclusion, data at smaller q 's than we have been able to achieve are needed.

In Fig. 3 we give the q -dependence of the relative damping coefficient for two coverages at 26°C. Figure 3a shows the results for a coverage of 0.0135 molecules/ $\text{\AA}^2$ with a surface tension of 60.5 dynes/cm. The theoretical

curve is for zero surface viscosity and a film compressibility of 0.02. In Fig. 3b we give the results for a coverage of 0.0223 molecules/ $\text{\AA}^2$ with corresponding surface tension of 39 dynes/cm. The theoretical curve in this case is for an incompressible film at the interface. For q values above 10^3 cm^{-1} , the experimental results agree with the theoretical fit for both coverages. The systematic discrepancy between theory and experiment for the lower q 's is caused in part by an overestimate of the instrumental line-width due to our inability to completely isolate low frequency mechanical vibrations from our experimental set-up.

In Fig. 4 we present a summary of the temperature dependence of the real surface tension, the relative damping coefficient, and the area per molecule for both a full monolayer and for the low coverage side of the expanded-condensed transition region. It can be seen that the low coverage results extrapolate to the full monolayer values at $\sim 42^\circ\text{C}$. It is of interest to note that, for a full monolayer, an 8 $\text{\AA}$ jump in the area per molecule occurs within an increment of one degree around 41°C . This provides evidence that the expanded-condensed phase transition is in fact the chain melting one observed at 41.5°C in bulk DPPC (15,16). The magnitude of the jump is consistent with bulk x-ray data (15).

We observe no increase in the compressibility of the monolayer at the onset of the expanded - condensed transition as the temperature increases. This and the jump in area per molecule lead us to conclude that the system does not exhibit critical behavior.

It is known that a second phase transition, the so called pretransition, occurs in bulk DPPC systems at 34.5°C (16-18). We observed such a transition in the monolayers. Our evidence for that is the abrupt change in the slope

of the surface tension vs. temperature isochore as shown in Fig. 5.

Albrecht et.al. have recently published a phase diagram of DPPC monolayers (19) which exhibits an isotropic-anisotropic fluid transition within the expanded state. We should like to point out that this is not the same transition shown in Fig. 5. According to Ref. 19 the isotropic-anisotropic transition takes place at surface pressures above 10 dynes/cm as compared with 7.4 dynes/cm in our case. In addition, the transition line of Ref. 19 moves towards high surface pressures at high temperatures and one would have to observe a second change of phase back to the isotropic state. No such second transition was seen. The fact that at low coverage the transition occurs at a lower temperature is consistent with weaker cooperative interaction at lower densities. The isotropic-anisotropic fluid transition described in Ref. 19 appears as a discontinuous decrease in the monolayer compressibility as the surface coverage is increased. Such a change should lead to a discontinuous decrease of the ripplon damping which, within the accuracy of our data, we do not observe.

We observe that the film loses stability in the condensed phase about 34°C for surface tensions lower than about 30 dynes/cm. The temperature dependence of this instability may possibly be related to the "pretransition".

5. Conclusion

The initial results described above show that scattering of light by ripplons can be a useful tool for probing the rheological and phase transition aspects of insoluble monolayers at the interfaces. Further work is in progress in our laboratory.

REFERENCES

1. Gaines, G. L., Insoluble Monolayers at Liquid-Gas Interfaces, (Interscience, New York), 1966
2. Lucassen, J. and Hansen, R. S., J. Coll. Interf. Sci. 22, (1966) 32.
3. Bouchiat, M. A. and Meunier, J., Polarisation, Matiere, et Rayonnement, (P.U.F.) 1969.
4. Herpin, J. C. and Meunier, J., J. Physique 35 (1974) 847.
5. Prosperetti, A., Phys. Fluids 19 (1976) 195.
6. Bouchiat, M. A. and Meunier, J., J. Physique 32 (1971) 561.
7. Hard, S., Hammerins, Y., and Nilsson, O., J. Appl. Phys. 47 (1976) 2433.
8. Lean, E. G. in Progress in Optics (Wolfe, E., edit. North-Holland) 1973.
9. Langevin, D., and Bouchiat, M. A., C. R. Acad. Sc. B, Paris 272 (1971) 1422.
10. Brochard, F. and de Gennes, P. G., Parmana Suppl. 1 (1975) 1.
11. Landau, L. D. and Lifshitz, F. M., Fluid Mechanics (Addison-Wesley, Mass.), 1959.
12. Levich, V. G., Physicochemical Hydrodynamics, (Prentice Hall, N. J.), 1962.
13. Phillips, M. C., Chapman D., Biochem. Biophys. Acta 163 (1968) 301.
14. Hayashi M., Muramatou T., Hara I., Seimiya T., Chem. Phys. Lipids 15 (1975) 209.
15. Rand R. P., Chapman D., Larsson K., Biophys. J., 15 (1975) 1117.

16. Janiak M., J., Small D. M., Shipley G. G., Biochemistry 15 (1976) 4575 and references therein.
17. Uhing M. C., Chem. Phys. Lipids 14 (1975) 303.
18. Gally H. U., Niederberger W., Seelig J., Biochemistry 14 (1975) 3647.
19. Albrecht O., Gruler H., Sackmann E., J. Physique 39 (1978) 301.

FIGURE CAPTIONS

1. Experimental set-up.
2. Apparent surface tension and damping as a function of surface coverage for 32.4°C.
3. Wave vector dependence of relative damping coefficient at 26°C.
 - a) coverage of 0.0135 molecules/Å² (expanded phase),
 - b) coverage of 0.0223 molecules/Å² (condensed phase); the solid lines are theoretical fits for zero surface viscosity and for an incompressible film, respectively.
4. Temperature dependence of monolayer parameters. Solid circles are for full monolayer, open circles for the low coverage side of the expanded-condensed transition region.
5. Surface tension isochore showing the "pretransition". Only some of data points are shown. The solid line represents the average behavior of data.

XBL 786-9199

Fig. 1

XBL 786-9203

Fig. 2

XBL 786-9202

Fig. 3

XBL 786-9201

Fig. 4

XBL 786-9220

Fig. 5

XBL 786-9201

Fig. 4

XBL 786-9220

Fig. 5

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720