Viscoelasticity of monolayers of n-pentadecanoic acid: a light scattering study

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Abstract. The viscoelastic properties of monolayers of n-pentadecanoic acid at the air–water interface have been studied using surface light scattering. The monolayers displayed first-order liquid-condensed to liquid-expanded transitions: the surface properties reported are those of well defined, reproducible monolayer states. Two viscoelastic moduli were determined: for shear transverse to the surface and for uniaxial dilation in the surface. For experiments both above and below the triple point the surface viscoelasticity was found to depend upon the monolayer phase in a complex fashion. Both moduli displayed viscoelastic relaxation, the strength and timescales being different for the two moduli, as well as depending upon the monolayer state. At one point in the phase diagram it was shown that the high-frequency dilational viscosity measured by light scattering could be identified with the conventional surface shear viscosity. The results confirm the complexity of the viscoelastic behaviour of molecular films, which is not adequately represented by a single surface viscosity.

1. Introduction

Molecular monolayers spread at fluid interfaces are of both scientific and technological interest. Their relevance ranges from modelling bio-membranes to use as precursors of multilayer structures (Langmuir–Blodgett films) with interesting optical and electronic properties. The physical organisation or phase state of the monolayer is fundamental to many areas, so that the phases and transitions of these molecular systems have been the subject of much interest. The commonest experimental approach to the study of these phases has been the surface pressure–area (π–A) isotherm. However it is now accepted that this may not reflect all of the phase changes, so attention has turned to other physical properties, including surface elasticity and viscosity. As well as having the potential to reveal more details of phase changes, surface viscoelasticity should be useful in studying the nature of the various phases involved. A relatively new technique, sensitive to viscoelastic properties of a spread monolayer, is light scattering by thermally excited capillary waves on a liquid surface.

Laser light scattering (LLS) has been used to study monolayers for about a decade [1]. It is basically non-invasive, making it an ideal probe of these delicate systems. In parallel with advances in methods for film preparation and manipulation, LLS techniques have been steadily refined, improving the reliability of inferences drawn from

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such experiments. The present paper describes a more rigorous approach to light scattering from molecular monolayers than has been evident in most previous work. There are two distinguishing features of this work. Firstly the monolayers are pure and well equilibrated, as demonstrated by the flatness of the isotherms in the liquid-expanded/liquid-condensed transition region, ensuring that the monolayer properties are those appropriate to reproducible, well defined phases. In only one other LLS study has such equilibration been demonstrated [2]. Secondly the light scattering data have been analysed by a more powerful procedure than that commonly used, the surface properties being *directly* extracted from the observed data [3]. This approach, using exact theoretical formulae rather than approximations, should yield optimal estimates of the surface properties, limited only by the precision of the experimental data and the intrinsic limitations of the light scattering methods.

The present study involves pentadecanoic acid (PDA), a fully saturated fatty acid for which the π–A isotherm has been well established [4]. Recent observations [4,5] with conventional techniques show that the liquid-condensed/liquid-expanded phase transition is first order, like the liquid/gas transition. It is this demonstration of the simplicity of these transitions which has led to PDA becoming a basic reference material for monolayer studies. We have previously reported light scattering phenomena relating to the various phase transitions observed for PDA monolayers, demonstrating phase coexistence in these transitions [6]. The present paper concentrates upon the viscoelastic properties of monolayers both above and below the triple point (T_t) of PDA.

2. Experimental methods

2.1. Monolayer methods

The Langmuir trough was designed with the light scattering experiments in mind: in particular its large area (18×23 cm) obviated problems which could arise from curvature of the meniscus, and it was shallow to damp out any long-wavelength surface waves driven by acoustic or building vibrations. The monolayer temperature was maintained stable, both spatially and temporally, to better than $0.1\,^\circ$C. The humidity of the enclosure surrounding the trough was close to 100%. Conventional surface pressure measurements were made using a platinum foil Wilhelmy plate. A fuller description of the monolayer apparatus has been published [6].

It has been suggested that ultra-high purity of materials and environment are required to permit first-order phase transitions to be observed in monolayers [4]. The procedures for achieving adequately low levels of residual contamination have been described elsewhere, together with the methods used to generate isotherms [6]. With highly repurified PDA and careful technique it proved possible to reproduce the flat LC/LE transitions indicative of a first-order transition [7].

2.2. Light scattering

The thermally roughened surface of a fluid can be Fourier decomposed into surface or capillary modes which scatter light. The spectrum of the light quasi-elastically scattered by a capillary mode of wavenumber q reflects the temporal evolution of the

mode, expressed by the wave frequency ω $(= \omega_0 + \Gamma)$. It is influenced by four surface properties, comprising two viscoelastic moduli [8]:

$$\begin{aligned}\gamma &= \gamma_0 + i\omega\gamma' \\ \varepsilon &= \varepsilon_0 + i\omega\varepsilon'.\end{aligned} \tag{1}$$

Here γ, governing shear normal to the surface, comprises the surface tension γ_0 and the transverse shear viscosity γ'. Similarly ε is the in-plane dilational modulus including the elastic modulus ε_0 (classically $= -A \, d\gamma_0/dA$) and the dilational viscosity ε'. More precisely, for uniaxial stresses such as those caused by capillary waves or by monolayer compression in a single-barrier Langmuir trough (as here), the dilational modulus is the sum of the bulk modulus (K) and that for shear (S):

$$\varepsilon = K + S. \tag{2}$$

This applies to both elastic and viscous portions of ε. The theoretical spectrum of light scattered by thermally excited capillary waves, $P(\omega, q \mid \gamma, \varepsilon)$, can be written explicitly in terms of the above surface moduli and the bulk properties of the subphase [9].

The laser light scattering spectrometer has been described in detail elsewhere [6, 10]. The spectral information was obtained in the time domain by photon correlation, yielding the Fourier transform of the spectrum $P(\omega)$ of waves of experimentally selected q.

To date two distinct approaches to data analysis have been applied to LLS data from molecular surface films.

(i) One, based on the fact that the spectrum is approximately Lorentzian, involves fitting the observed correlation functions with

$$g(\tau) = B + A \cos(\omega_0 |\tau| + \phi) e^{-\Gamma\tau} h(\tau) \tag{3}$$

where the phase term ϕ allows for the deviations of $P(\omega)$ from a Lorentzian form, B and A are background and amplitude respectively, and $h(\tau)$ is an instrumental term [11]. Whilst this approach is reasonably simple computationally, its utility is limited by the difficulty of extracting four surface properties from two observables: the wave frequency (ω_0) and damping (Γ). Matching ω_0 and Γ by values computed assuming $\gamma_0(\omega) = \gamma_0(\text{eq})$ and $\gamma' = 0$ is necessary to demonstrate the validity of these assumptions, but not sufficient. Nor can $\varepsilon_0(\omega)$ and ε' thus derived be guaranteed to be unbiassed, as the constraints may affect their values. In general four physical properties cannot be uniquely determined from two observables. Despite these problems, this method has been widely used in previous LLS studies of monolayers [1, 2, 9, 12, 13]. Here it has only been used to provide estimates of ω_0 for discussion purposes.

(ii) In the present work, correlation functions were fitted with an exact analytical form in terms of the four surface properties [11, 14]:

$$g(\tau) = B + A \, \text{FT}[P(\omega, q \mid \gamma, \varepsilon)] h(\tau) \tag{4}$$

where $P(\omega, q \mid \gamma, \varepsilon)$ is the exact spectrum, and $\text{FT}[x]$ indicates the Fourier transform. Tests using simulated data have shown that, in general, the values of the surface properties thus found are unbiassed [3]. However, for certain combinations of surface properties the solution of the minimisation problem can apparently be ill-defined. One

such case, for $\varepsilon_0 \sim 12$ mN m^{-1}, is illustrated in figure 1; it is apparent that above their true values neither γ_0 and ε_0 strongly affects F, so that in the presence of noise (which would further blur the minimum) these properties might be overestimated. Analysis of simulated data has confirmed this possibility. Errors on the fitted parameters were estimated from the Hessian matrix computed by the fitting subroutine; simulations confirmed the reliability of these estimates [15]. The uniqueness and stability of this method of 'direct' analysis is discussed fully elsewhere [15]. Only one or two previous studies have used this approach (e.g. [14]).
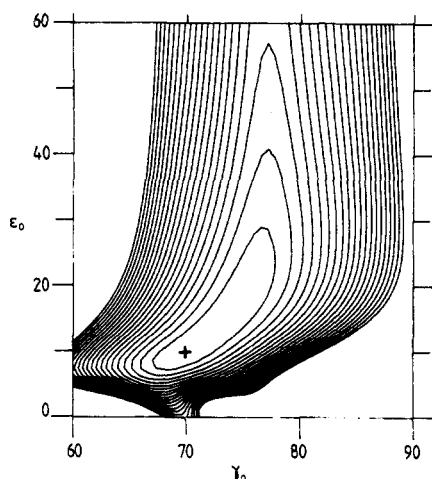

Figure 1. Contour plot of the region around the minimum of the sum-of-squares function, F, for a noise-free simulated correlation function generated with $\gamma_0 = 70$ mN m^{-1}, $\varepsilon_0 = 10$ mN m^{-1} (indicated by +), and $\gamma' = \varepsilon' = 0$. Twenty contour lines are drawn at equal intervals for $0.01 < F < 2$.

3. Results

A selection of classically measured isotherms are shown in figure 2. The transition regions between the liquid-expanded and liquid-condensed states are flat, indicating a first-order transition [7]. We will refer to the three two-dimensional phases as liquid-condensed (LC), liquid-expanded (LE) and gaseous, although there is still debate concerning their nature [16].

Light scattering experiments were carried out for several temperatures; to simplify the presentation we only show data for two monolayers, at temperatures (22.4 and 15.0 °C) above and below the triple point ($T_t \sim 17$ °C) of PDA. The higher temperature was selected to avoid excessively large ε_0 values at the dense end of the liquid-expanded region, which would have reduced the sensitivity to ε. The data are reported in terms of the four surface properties (γ_0, γ', ε_0, ε') extracted using the direct analysis with equation (4). Neither the transverse nor the dilational viscosity was constrained to be positive in the analysis of any of the present data. In both cases the few negative values observed are due to fluctuations, of quantities of very small magnitude, caused by noise on the observed correlation functions. Other data over a range of T quantitatively support all of the results shown.
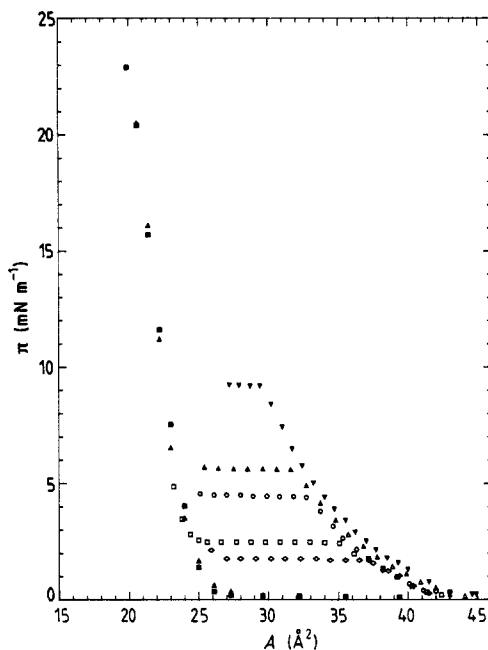
Figure 2. A selection of isotherms of PDA measured classically: ∇, 27.2 °C; $\triangle$, 23.5 °C; O, 22.4 °C; $\square$, 19.6 °C; $\lozenge$, 19.0 °C; $\blacksquare$, $\blacktriangle$, 11.5 °C. Those isotherms exhibiting a liquid phase (open symbols) were produced by expansion; note the flat first-order coexistence regions. Compression by successive addition was used at $T < T_t$ (full symbols).

To distinguish between light scattering and equilibrium values of the surface properties the former are written below as, for example, $\gamma_0(\omega)$ and the latter as $\gamma_0(\text{eq})$.

3.1. Monolayer at 22.4 °C

The classical and LLS estimates of surface pressure are shown in figure 3 as functions of molecular area (A). Based on $\pi(\text{eq})$ we assign the following ranges of molecular area to the various phases: $23 \lesssim A \le 32.5$ Å^2, LC/LE coexistence; $32.5 < A \le 42$ Å^2, liquid expanded; $A > 42$ Å^2, liquid/gas coexistence. Over most of the isotherm the two estimates of π appear quite compatible. However, towards the expanded end of the LE region $(A > 38$ Å$^2)$ the LLS tensions generally exceeded the classical estimates, resulting in $\pi(\omega)$ being lower than $\pi(\text{eq})$. In the liquid/gas coexistence region the two estimates seem to converge again.

The corresponding transverse shear viscosity, γ', is also shown in figure 3. The behaviour of this viscosity divided into two regimes, the change coinciding with passage from the LE phase to the LC/LE coexistence region. In the two-phase region γ' was compatible with zero; there might have been a slight tendency for it to rise at $A < 25$ Å^2 although the magnitude is very small, $\sim 10^{-6}$ mN s m^{-1}. At larger molecular areas γ' increased, becoming significant for $A \ge 37$ Å^2. It may reach a maximum for very expanded liquid states before falling slightly in the liquid/gas coexistence region. However, even the largest observed values are quite small $(\sim 10^{-5}$ mN s m$^{-1})$ so that such fine details may not be entirely reliable.
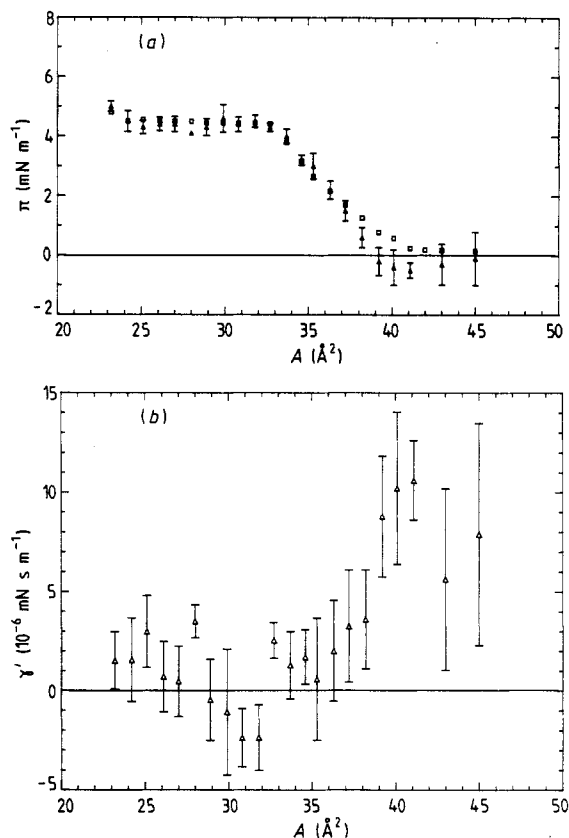
Figure 3. The transverse shear modulus of a PDA monolayer at 22.4 °C: (*a*) comparison of classical (□) and LLS (△) estimates of surface pressure, and (*b*) transverse shear viscosity. Light scattering at $q = 636$ cm^{-1}.

The dilational modulus influences the capillary waves only indirectly, via the coupling of transverse and longitudinal waves [9]. The effects of ε upon the spectrum of the scattered light are thus small, making it difficult to determine this modulus very precisely by LLS except for $\varepsilon_0 \lesssim 0.3\gamma_0$, a resonance in the response occurring about $0.16\gamma_0$ [9]. When ε_0 is much larger the precision of extraction of both ε_0 and ε' is poor.

The measured values of elastic modulus ε_0 and the viscosity ε' are shown as functions of molecular area in figures 4 and 5. The classical elastic values were obtained from the logarithmic derivative of a spline fit to the classical isotherm (figure 3). In both coexistence regions the π–A isotherm was flat, so that $\varepsilon_0(\text{eq}) = 0$.

In the LE phase ($32.5 < A \le 42$ Å^2) the fitted values of $\varepsilon_0(\omega)$ consistently exceeded the classical estimates at larger molecular areas, the two variations converging as the molecular area was reduced toward the LC/LE coexistence region. Throughout the LE phase $\varepsilon_0(\omega)$ varied smoothly with molecular area; these estimates should be quite accurate since their magnitude was relatively small. This was confirmed by the small errors returned by the fitting routine.

As the liquid/gas coexistence region ($A > 42$ Å^2) was approached $\varepsilon_0(\omega)$ became constant around 17 mN m^{-1} whilst $\varepsilon_0(\text{eq}) \to 0$. It was found that continued expansion,
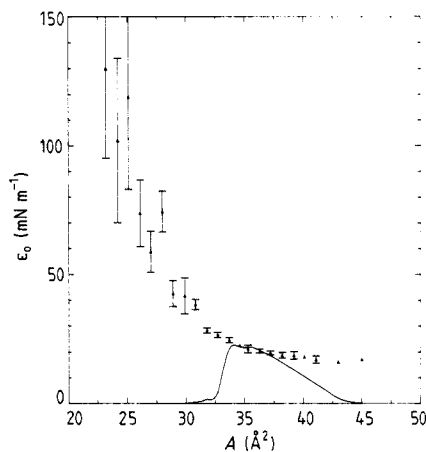
Figure 4. LLS estimates of the dilational elastic modulus ε_0, for the monolayer of figure 3. The full line indicates the variation of the classical values.
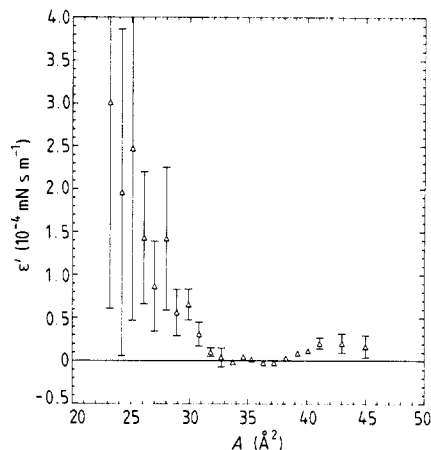
Figure 5. The dilational viscosity for the monolayer of figure 3. Note the small values of ε' in the LE phase.

beyond the areas shown, resulted in erratic fluctuations between this value of $\varepsilon_0(\omega)$ and one appropriate to a clean subphase $(\varepsilon_0(\omega) = 0)$. These fluctuations were ascribed to the motion of quite large domain structures (~ 1 cm); a more detailed discussion has been published [6].

In the LC/LE coexistence region ($A < 32.5$ Å^2) $\varepsilon_0(\omega)$ remained large, unlike the classical estimate. The smooth variation of this elastic modulus found in the LE phase was replaced by a tendency to fluctuate. While the estimates of such large values of ε_0 must be intrinsically uncertain, the observed fluctuations were greater than expected. As with the liquid/gas coexistence region these excess fluctuations have been interpreted in terms of coexistence effects [6]. The data shown are the averages of fitted values from 10 separate correlation functions. The average $\varepsilon_0(\omega)$ rose with increasing surface concentration, reflecting the increasing fraction of LC phase present in the region illuminated by the laser beam.

The dilational viscosity ε' appeared to be very small ($\lesssim 10^{-5}$ mN s m^{-1}) throughout most of the LE region (figure 5). Within the LC/LE coexistence region ε' increased steadily by more than an order of magnitude as the area was decreased, reaching a value of $\sim 2 \times 10^{-4}$ mN s m^{-1} at the lowest molecular area. Towards the expanded end of the LE phase, and into the liquid/gas coexistence region ε' rose, becoming roughly constant at $\sim 2 \times 10^{-5}$ mN s m^{-1} above 41 Å^2.

The dilational viscosity ε' is phase dependent: it increased rapidly as the monolayer was compressed in the LC/LE coexistence region. Another interesting aspect of these data is that over the region of the isotherm where ε' was near zero the light scattering estimates of ε_0 were very close to the classical estimates. These aspects will be discussed below in detail.

3.2. Isotherm at 15.0 °C

For these data, obtained below the triple point of the monolayer, the surface properties are presented as a function of surface concentration Γ_s ($= 1/A$), allowing data at large molecular areas to be displayed clearly. This isotherm was generated by successive
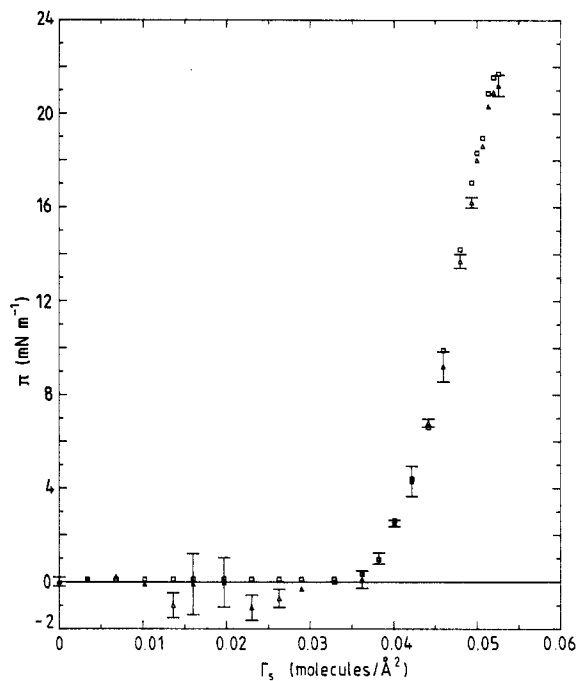
Figure 6. Comparison of classical ($\square$) and LLS ($\triangle$) estimates of surface pressure for a monolayer at 15 °C. Light scattering at $q = 617$ cm^{-1}.

additions of spreading solution, rather than by barrier expansion, so that the data are linearly spaced in Γ_s.

In figure 6 LLS estimates of the surface pressure, $\pi(\omega)$, are compared with classical values, $\pi(\mathrm{eq})$. In two regions of the plot notable discrepancies occurred.

(i) At low surface pressures ($\pi(\mathrm{eq}) = 0.11$ mN m^{-1}) in the condensed/vapour coexistence region estimates of $\gamma_0(\omega)$ were not very reproducible, experiments on different monolayers yielding different values. For the data reported here $\gamma_0(\omega)$ tended to slightly exceed the value for a clean water surface, resulting in a negative surface pressure. However in other cases positive pressures were observed. The error estimates from the fitting routine were larger in this region than elsewhere.

(ii) In the condensed phase $\pi(\mathrm{eq})$ consistently exceeded $\pi(\omega)$ at high surface pressures. The difference increased with Γ_s, reaching ~ 0.5 mN m^{-1}. Although these discrepancies were small they were observed in all comparable experiments.
We will discuss these deviations below.

The associated transverse shear viscosity is shown in figure 7. At very low surface concentrations γ' was zero, consistent with a clean water surface. As Γ_s increased above ~ 0.005 molecules/Å^2 the transverse viscosity rose to $\sim 10^{-5}$ mN s m^{-1}, before decreasing gradually on further compression toward the condensed phase. Within this phase γ' was small ($\sim 10^{-6}$ mN s m^{-1}). The occurrence of the larger γ' values within the condensed/vapour coexistence region, rather than in the condensed phase resembles behaviour found for glycerol monoöleate (GMO) [14].

The dilational modulus also behaved unexpectedly in the condensed/vapour coexistence region. Figure 8 compares the dynamic elastic modulus with its classical counterpart. At low surface concentrations $\varepsilon_0(\omega) = \varepsilon_0(\mathrm{eq}) \equiv 0$ as expected, but as Γ_s
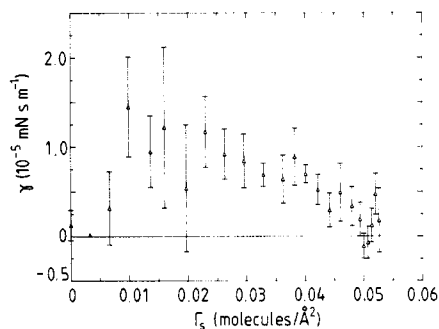
Figure 7. Transverse shear viscosity γ' as a function of molecular concentration Γ_s for the monolayer of figure 6.

was increased beyond ~ 0.013 molecules/Å^2 a substantial increase in $\varepsilon_0(\omega)$ occurred, quite large values being reached. The average $\varepsilon_0(\omega)$ here was 48 ± 4 mN m^{-1}. In this region, corresponding to $A \lesssim 77$ Å^2, the damping of the observed correlation functions visibly exceeded values observed at larger Γ_s. Further compression caused both $\varepsilon_0(\omega)$ and $\varepsilon_0(\text{eq})$ to rise rapidly. The insensitivity of LLS to ε at high values of ε_0 is reflected in the large error bars and fluctuations of $\varepsilon_0(\omega)$ in this region. Close to, and in the collapse region of the solid phase $\varepsilon_0(\omega)$ and $\varepsilon_0(\text{eq})$ appeared reasonably compatible, although the precision of $\varepsilon_0(\omega)$ is inevitably poor.
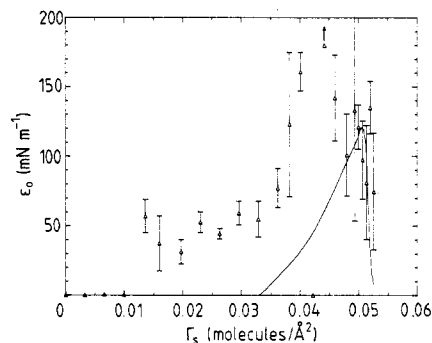

Figure 8. Dilational elastic modulus ε_0 as a function of molecular concentration Γ_s for the monolayer of figure 6. The point marked with an upward arrow corresponds to an essentially infinite value ($> 10^3$ mN m^{-1}). The full line indicates the classical variation.
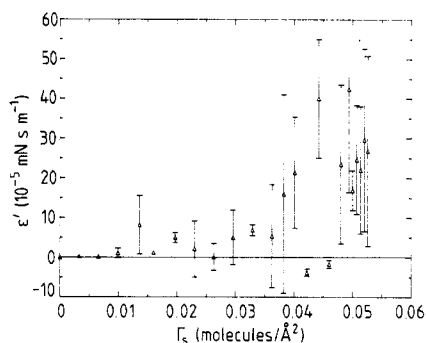
Figure 9. Dilational surface viscosity ε' as a function of molecular concentration Γ_s for the monolayer of figure 6.

The variation of the dilational viscosity ε' with surface concentration is shown in figure 9. As with the other surface properties, at low concentrations the values found for the monolayer were comparable with that for a clean surface ($\varepsilon' = 0$). However ε' increased at that Γ_s at which the abrupt increase in $\varepsilon_0(\omega)$ was observed, reaching an average value of $(4.9 \pm 1.0) \times 10^{-5}$ mN s m^{-1}. In the solid phase ε' rose monotonically with concentration by an order of magnitude, reaching $\sim 2 \times 10^{-4}$ mN s m^{-1} at about the collapse point. The few small negative values found for ε' in this region are just due to the difficulties of determining this viscosity when $\varepsilon_0(\omega)$ is large in magnitude.

4. Discussion

The discussion concentrates on the contrasting behaviour of the moduli γ and ε for the two isotherms.

4.1. Viscoelastic relaxation

The surface properties may be viscoelastic in nature. There is as yet no molecular theory of the viscoelastic response of interfacial molecular films. We therefore assume the simplest frequency-dependent model, the viscoelastic or Maxwell fluid. This assumption can partially be justified by recent demonstrations that this model adequately describes the observed relaxation of the transverse shear modulus of mono- and bilayers of glycerol monoöleate [14, 17], and is consistent with the dilational modulus in the former [14]. Three-dimensional rheological bodies usually display much more complicated behaviour, but can always be modelled by appropriate combinations of Maxwell elements [18]. There is no reason to suspect that this is not true of viscoelastic molecular films.

Adopting the usual notation [18], the response to oscillatory stress of frequency ω is governed by a complex modulus

$$G(\omega) = G'(\omega\ ) + \mathrm{i}G''(\omega) \tag{5}$$

which for a Maxwell fluid is given by

$$G'(\omega) = G(\mathrm{eq}) + G\frac{\omega^2\tau^2}{(1\ +\ \omega^2\tau^2)} \tag{6}$$

$$G''(\omega) = G\frac{\omega\tau}{(1\ +\ \omega^2\tau^2)}. \tag{7}$$

Here τ is the timescale and G the strength of the relaxation involved. The elastic response is represented by the real part of $G(\omega)$ (the storage modulus), $G(\mathrm{eq})$ being its equilibrium ($\omega \to 0$) value. The imaginary component (the loss modulus) describes the energy dissipation or viscous response.

Comparison of the forms of equations (1) and (5) shows that the interfacial moduli can be identified with the complex modulus $G(\omega)$:

$$\left.\begin{array}{c} \gamma_0 + \mathrm{i}\omega\gamma' \\ \varepsilon_0 + \mathrm{i}\omega\varepsilon' \end{array}\right\} \equiv G'(\omega) + \mathrm{i}G''(\omega). \tag{8}$$

Thus $\gamma_0(\mathrm{eq})$, the equilibrium or classical value of the tension, and $\varepsilon_0(\mathrm{eq})$, the dilational elastic modulus, correspond to $G(\mathrm{eq})$ for their respective moduli. The surface viscosities correspond to $G''(\omega)/\omega$.

For a single Maxwell relaxation process the elastic modulus will equal $G(\mathrm{eq})$ for perturbations of frequency $\ll 1/\tau$, while the viscosity will be at its maximal value $G\tau$, both being essentially constant. For ω well above the inverse relaxation time, $G'(\omega) = G(\mathrm{eq}) + G$ while the viscosity $\propto \omega^{-2}$. These points help in interpretation of certain aspects of the present results. In particular if only one Maxwell process affects a given modulus then its timescale τ can be estimated using

$$\tau = \frac{G'(\omega) - G(\mathrm{eq})}{\omega G''(\omega)} \tag{9}$$

given $G'(\omega)$ and $G''(\omega)$ at the single frequency ω and $G(\mathrm{eq})$. The oscillatory perturbation is just the observed capillary mode, so that we take ω to be the wave frequency ω_0.

As already noted, complex viscoelastic behaviour can be represented by an ensemble of Maxwell elements, each characterized by a particular relaxation time τ. If all the relaxation times were greater than $1/\omega_0$ then the above method would yield some average τ. If one process were faster and another slower than $1/\omega_0$ the procedure used would underestimate the larger τ, that involved in the observed relaxation.

4.2. Monolayer at 22.4 °C

4.2.1. The transverse shear modulus γ. This is the first LLS study of the surface properties of PDA in which non-zero values of γ' have been demonstrated. The interpretation of ω_0 and Γ in terms of the four surface properties is beset by too many imponderables to make detailed discussion of earlier reports worthwhile (c.f. [13]). It has been common to constrain $\gamma' = 0$ in this interpretation [2, 12, 13]. The present data suggest that for $T > T_t$ this assumption may be acceptable within the LC/LE coexistence region and over part of the LE region. We have not investigated the effects of this constraint upon the other surface properties, but as γ' primarily acts to increase the wave damping, it seems most likely to be ε_0 and ε' (which also affect Γ) which would be affected.

Over the LC/LE coexistence region and part of the LE region ($A \leq 37$ Å^2) the classical and light scattering tensions agree, while $\gamma' \sim 0$ (figure 3). Now a low surface viscosity could arise from either of two causes: a slow relaxation ($\omega_0 \tau \gg 1$) or a low strength, G. However, in the former case the storage modulus would exceed its equilibrium value by $\sim G$ (c.f. equation (6)); the agreement of $\gamma_0(\omega)$ and $\gamma_0(\mathrm{eq})$ indicates that G must be negligible. Even at low frequency the viscosity γ' must be very small.

The tension $\gamma_0(\omega)$ was consistently above $\gamma_0(\mathrm{eq})$ at molecular areas approaching the liquid/gas coexistence region, corresponding with the largest values of the transverse shear viscosity ($\sim 10^{-5}$ mN s m^{-1}). $\Delta\gamma_0$ ($\equiv \gamma_0(\omega) - \gamma_0(\mathrm{eq})$) and γ' increase in parallel, reaching their respective maxima at about the same A, suggesting that they are related.

In the absence of direct observations of the frequency dependence of $\gamma_0(\omega)$ and γ', we cannot be sure that there is only one significant relaxation process, nor that that process can be described by a Maxwell fluid behaviour. However some insight into the likely timescales involved can be gained by positing a single Maxwell fluid process and using equation (9) to estimate τ. For example, at $A = 40$ Å^2 we have $\Delta\gamma_0 = 1$ mN m^{-1} and $\gamma' = 10^{-5}$ mN s m^{-1} (figure 3), while the capillary wave frequency was about 1.4×10^5 s^{-1}: equation (9) yields $\tau \sim 5.2$ μs. The strength of the relaxation is ~ 2.9 mN m^{-1}. The poor precision of $\Delta\gamma_0$ and γ' precludes detailed analysis of the A dependence of τ: within errors it seemed constant at about 5 μs. More precise experiments are needed to substantiate the data. Studies of the frequency (i.e. q) dependence of γ would be useful: we note that γ' is not far below its low-frequency value ($G\tau$) of $\sim 1.5 \times 10^{-5}$ mN s m^{-1}.

In summary, the viscosity γ' is negligible in the more condensed states, whereas it is of measurable magnitude in the expanded phases. Such behaviour is counter-intuitive, running against the association of greater values of viscosity with increasing

inter-molecular interactions. However the present γ' values relate to rather high-frequency perturbations. As little is known of the underlying molecular mechanisms and relaxation processes further speculation on this topic seems premature.

4.2.2. The dilational modulus ε. The present data are compatible with those of the only previous study involving well equilibrated monolayers [2]. The assumption made in that work that γ' was negligible was probably justifiable over most of the isotherm studied.

The present results show, for the first time, that ε' depends strongly on the monolayer phase (figure 5). The correlation of a rapid rise of ε' with the onset of the LC/LE transition was confirmed at various temperatures, for which the relevant values of both molecular area and ε_0 differed substantially. The viscosity ε' also rose somewhat on expansion into the liquid/gas two-phase region. The observation of variations of the magnitude of ε' with monolayer phase suggests that the measured values are real, and relate to processes within the monolayer. This point is significant since this viscosity is rather difficult to measure by LLS, due to the indirectness of its effects upon the capillary waves.

The various discrepancies observed between $\varepsilon_0(\omega)$ and $\varepsilon_0(\text{eq})$ (figure 4), and the finite values of ε' (figure 5) suggest that viscoelastic relaxation processes affect the dilational modulus. These processes may well vary with monolayer state: like ε', $\Delta\varepsilon_0$ ($\equiv \varepsilon_0(\omega) - \varepsilon_0(\text{eq})$) depends upon the film phase. We briefly review the evidence that viscoelastic relaxation affects ε.

(i) Within the LC/LE coexistence region, where ε' rose rapidly and systematically on monolayer compression, the Wilhelmy plate tension was observed to change momentarily following a change in A, before relaxing towards its previous, equilibrium value. The decay was approximately exponential, as for a Maxwell fluid, with time constant longer than seconds. Now $\gamma_0(\omega) = \gamma_0(\text{eq})$ in this region so that this variation derives from a relaxation of ε, rather than of γ. The slow decay observed implies that at least one relaxation must have $1/\tau < 1\ \text{s}^{-1}$. This probably arises from interchange of molecules between coexisting phase-separated regions. The strength of the relaxation (G) exceeds $25\ \text{mN m}^{-1}$, increasing as A is reduced. This behaviour was not apparent in the pure LE phase.

(ii) The region $33 < A \leq 37\ \text{Å}^2$ in the LE phase where $\varepsilon' \to 0$ (figure 5) coincided exactly with the region where $\Delta\varepsilon_0$ was very small or zero. From the arguments used above for the case of $\gamma' = 0$, the strength of any relaxation affecting ε must be very small here.

(iii) At larger molecular areas, in the expanded LE phase and the liquid/gas coexistence region, $\varepsilon_0(\omega)$ systematically exceeded $\varepsilon_0(\text{eq})$ and the viscosity ε' became significant. In this region there was no apparent relaxation of the Wilhelmy plate tension, so any relaxation must be significantly faster than in the LC/LE case.

Comparisons of the ε' data with other estimates of surface viscosity (figure 10) are helpful in elucidating the mechanisms involved. Plotting ε' as a function of π facilitates comparison with other estimates of surface viscosity and emphasizes the rapid rise in ε' through the LC/LE transition. Unfortunately there are no data which are really comparable with the 22.4 °C results, and so LLS results for 19 and 26.5 °C are shown. The extremely small values of ε' are substantiated by recent estimates of ε' in the LE phase for myristic acid (13 CH_2 unit chain) at 20.2 °C [13].

Comparisons are made with two classical measurements of surface shear viscosity. The data seem reasonably consistent. The surface viscosity of PDA presumably lies
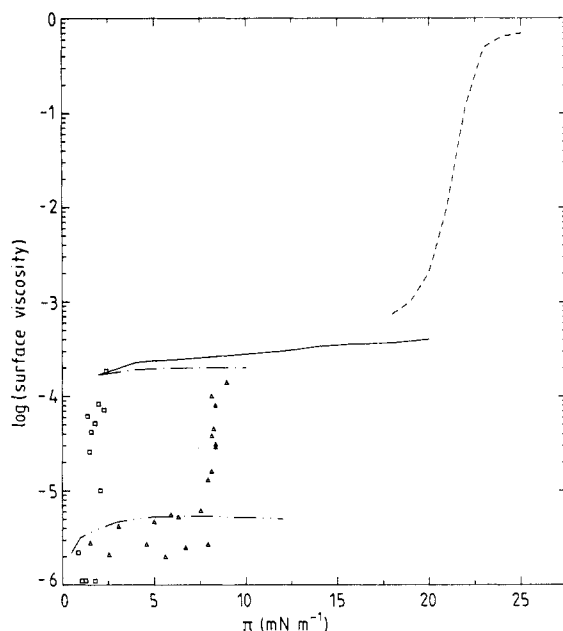
Figure 10. A comparison of various measurements of the surface viscosities of fatty acids. LLS ε' data shown include PDA at 19 °C ($\square$) and 26.5 °C ($\triangle$) and myristic acid [13] at 20.2 °C (— $\cdot$ $\cdot$ —). Torsion pendulum data for PDA [19] at 25 °C are shown (— — —), as are canal viscometer values [20] for myristic (— $\cdot$ —) and palmitic acids (———) at 20 °C.

between the canal viscometer data for myristic and palmitic (15 CH_2 units) acids. The classical values for all the acids agree over a wide range of π, encompassing LE (myristic), LC (pentadecanoic) and condensed (below T_t, palmitic) phases, suggesting that all respond to low-frequency shear strain similarly. At the only point of comparison— the condensed end of the LC/LE coexistence region—the present LLS data on ε' at both 19 and 26.5 °C agree with these classical results.

The LLS ε' results are thus consistent with comparable data. They continue smoothly into the canal viscometer results at the dense end of the LC/LE coexistence region. Viscoelastic relaxation of ε occurs in this two-phase region for PDA, τ being quite large. Thus the light scattering ε' should be smaller than at low frequencies, as $\varepsilon' \propto \omega^{-2}$ for $\omega \gg 1/\tau$ s^{-1}. The agreement between the low-frequency estimates of surface viscosity and those from high-frequency perturbations thus appears anomalous. However ε measured in LLS experiments, and from the π–A isotherm (involving uniaxial compression) is the sum of bulk and shear moduli, K and S (equation (2)), whereas classical viscometry measures the shear viscosity alone. The apparent dilemma is resolved if the slow relaxation evident in ε_0 is attributed to the bulk component alone. Any bulk viscosity would be quite negligible at light scattering frequencies: at $\omega_0 \sim 10^5$ s^{-1} the viscous part of K would be $\sim 10^{-10}$ times its low-frequency value for $\tau \sim 1$ s. Only the shear component can contribute significantly to that ε' which influences the capillary waves. The flatness of the present isotherms in the LC/LE transition implies that the equilibrium parts of both K and S be zero. This has recently been explicitly demonstrated for S [21]. Thus S at low frequencies is purely viscous. The agreement of ε' with the low-frequency surface shear viscosity

shows that any relaxation affecting the shear component must be faster than ω_0^{-1}.

The rise in ε' in the LC/LE coexistence region may be related either to the increasing fraction of the surface occupied by LC domains of high intrinsic viscosity, or to increasing inter-domain interaction as the domain separation falls. The latter hypothesis seems somewhat more plausible if ε' is essentially a shear viscosity; viscous domains in an ambient fluid monolayer could still respond to shear stress. The LC domains are much smaller than the illuminated region [6], so that LLS is responding to a local average monolayer state rather than sensing single-phase behaviour.

This positive identification of the surface viscosity ε', at least at one point of the isotherm, with one of its components is the first of its kind, and marks a distinct advance. Unfortunately it emphasizes the composite nature of the modulus ε, which will be subject to more than one relaxation process, even if only a single process affects each of K and S. For example, the slow inter-domain diffusion process discussed above, which determines the observed relaxation of ε_0, cannot be involved in the observed dilational viscosity ε'. Therefore the simple procedure of section 4.1 cannot yield a sensible estimate of the relaxation time involved.

All we can conclude from the present data is: (a) in the LC/LE two-phase region there is at least one slow relaxation affecting the bulk modulus, while, at least at the dense end of this region, the shear modulus shows no evidence of any relaxation with $\tau < 1/\omega_0$, (b) in dense LE states any relaxation of ε is of negligible strength and (c) in the expanded LE phase and the liquid/gas coexistence region a relaxation occurs with $1/\omega_0 < \tau < 1$ s. The latter conclusion may be supported by apparent frequency dependence of $\varepsilon_0(\omega)$ at lower q than the present [2].

4.3. Monolayer at 15 °C

The data for monolayers at temperatures below the triple point for PDA (figures 6–9) are the first LLS observations in this regime. They offer an interesting contrast to the data at higher temperatures. It is most straightforward to conduct the discussion in terms of the different behaviours of the various surface properties in different parts of the isotherm.

The isotherm naturally divides into three regions: one rather expanded ($\Gamma_s \lesssim 0.012$ molecules/Å^2), a normal condensed region ($\Gamma_s > 0.033$ molecules/Å^2) and an intermediate region in which certain anomalies of the surface properties were observed. While condensed and vapour phases will certainly have coexisted in this latter region, the two-phase region must extend to much larger areas. At the lowest Γ_s involved (0.0033 Å^2) the average separation of the PDA molecules would be less than their length so that the absence of condensation would be very unlikely. There is thus a change of behaviour within the coexistence region; in experiments on several different monolayers this change occurred at essentially the same Γ_s, corresponding to about the area of a PDA molecule lying upon the surface. It thus appears to be fundamental and intrinsic to the monolayer.

The transverse shear viscosity seems somewhat uncorrelated with the variations of the other surface properties. No changes in behaviour were evident at the boundaries between the monolayer regions, even at the onset of the condensed phase. We will briefly return to further discussion of γ' below.

4.3.1. The expanded monolayer.
The most expanded region can quickly be dealt with: within errors all of the monolayer properties, except perhaps γ', were entirely consistent with those of the free surface of the subphase. We have shown elsewhere [6]

that phase separation in these cold films involved rather small domains of condensed film, separated by the ambient gaseous phase. Any inter-domain interactions must evidently be very weak in this region.

4.3.2. Intermediate molecular areas. In the intermediate region ($0.012 < \Gamma_s < 0.032$ molecules/Å^2) both viscoelastic moduli show unusual variations.

The fluctuations of $\gamma_0(\omega)$ might have arisen from inhomogeneities in the monolayer. The connection of the behaviour of $\gamma_0(\omega)$ in this region with the nature of the monolayer does not seem straightforward and we will not discuss it further.

In its effects upon ε the monolayer, in which phase separation must have occurred, behaves as a homogeneous film. As discussed elsewhere [6], this suggests that the solid domains, which must be small to account for the lack of observed fluctuations in ε, interact to form some type of superstructure. This might be a 'super-lattice' as theoretically predicted [22], and observed in fluoresence microscopy of lipid monolayers [23], or perhaps a foam [24].

Here we concentrate upon the viscoelastic nature of the monolayer. The average values of $\varepsilon_0(\omega)$ and ε' were 48 ± 4 mN m^{-1} and $(4.9\pm1.0)\times10^{-5}$ mN s m^{-1} respectively. The discrepancy between $\varepsilon_0(\omega)$ and $\varepsilon_0(\text{eq})$ ($= 0$) shows that viscoelastic relaxation has occurred with G at least 48 mN m^{-1}. No relaxation was evident in recordings of the Wilhelmy plate tension so $\tau < 1$ s. It is not clear whether either or both K and S contribute to this relaxation, and we know of no low-frequency studies of the surface viscosity of PDA monolayers below the triple point.

Now τ must be $\gg 1/\omega_0$ unless G is astronomically large. We can estimate a plausible timescale via equation (9), using the average values of $\varepsilon_0(\omega)$ and ε' together with ω_0, here $\sim 1.3 \times 10^5$ s^{-1}: $\tau \sim 58$ μs. This lower limit on τ is both < 1 s and $\gg 1/\omega_0$. Confidence would be increased by observation of the frequency dependence of ε, but this will not be easy to obtain due to the difficulties in accurately determining ε' by light scattering. For such a τ the storage modulus $G'(\omega)$ ($\equiv \varepsilon_0(\omega)$) will equal G, and the low-frequency limit of ε' ($G\tau$) would be $\sim 2.8 \times 10^{-3}$ mN s m^{-1}.

This relaxation process does not seem to be connected to the condensed/gas coexistence *per se*, as the two-phase region must extend to much larger areas. It is thus not due to sublimation of PDA molecules from the domains of condensed film. We associate the relaxation with the super-structure of domains apparently formed in this region in the surface film [6], the monolayer as a whole acting as a viscoelastic fluid. The super-lattice of small domains observed in lipid films is susceptible to relatively slow perturbation [26], supporting this suggestion.

4.3.3. The condensed phase. In this region both $\gamma_0(\omega)$ and $\varepsilon_0(\omega)$ again differ from their classical counterparts. The two moduli are affected by different relaxation processes, so it is simplest to discuss them one at a time.

Both $\Delta\gamma_0$ and γ' vary sytematically with Γ_s. Similar effects have been reported for glycerol monoöleate monolayers [14], and for a DPPC monolayer at the oil/water interface [27]. In the case of GMO the explicit observation of frequency dependence of γ showed that viscoelastic relaxation was occurring [14]. Relaxation affecting the transverse shear modulus explains both the observed differences $\Delta\gamma_0$ and the finite values of γ'. The direct effects of γ upon the capillary waves should make it feasible to observe the variations of $\gamma_0(\omega)$ and γ'.

To investigate this point LLS data were recorded over a range of q for several monolayers compressed to the collapse point. Figure 11 shows the transverse shear
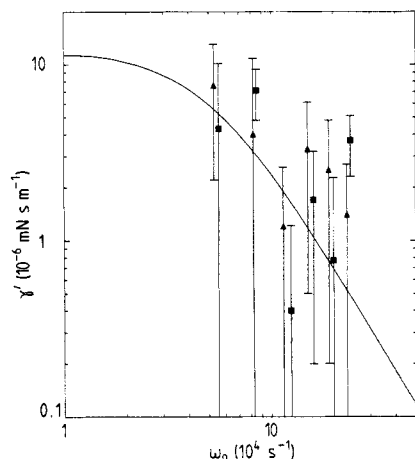
Figure 11. The transverse shear viscosity for two different fully compressed mono-layers at $T = 15\ ^\circ\mathrm{C}$ plotted as a function of capillary wave frequency ω_0. The full curve represents the variation expected for a Maxwell viscoelastic model, based on the data (at a single frequency) for the monolayer of figure 6 at the collapse point. See text for discussion.

viscosity for two such monolayers as a function of capillary wave frequency; γ' clearly falls with increasing ω_0, as expected on viscoelastic grounds. The corresponding $\Delta\gamma_0$ were rather scattered, being on average about 0.4 mN m^{-1}. The fitted values of γ' are very low and are thus subject to large errors, making further analysis difficult. The line shown is the variation expected for a Maxwell model having $\tau = 20\ \mu s$ and $G = 0.59$ mN m^{-1} (it is *not* a fit to the data). These parameters were estimated using the data for the most compressed state of figures 6 and 7, assuming a single Maxwell process. Substituting $\Delta\gamma_0$ (0.51 mN m^{-1}) and γ' (1.8 × 10^{-6} mN s m^{-1}), together with the capillary wave frequency (1.1 × 10^5 s^{-1}) into equation (9) yielded $\tau = 23\ \mu s$ (with large errors). The observed frequency dependence of γ' is clearly not inconsistent with the variation thus predicted from data for a single frequency from a separate monolayer; a relatively small reduction in τ, well within errors, would suffice to considerably improve the agreement with the observed data.

Thus two independent observations suggest the occurrence of a viscoelastic process. The best evidence comes from the frequency variation of γ', but this is quantitatively compatible with the discrepancies in the π–A plot.

As Γ_s decreases from the collapse point, the surface tension (and hence ω_0) rises, $\Delta\gamma_0$ falls and γ' increases in magnitude (figures 6 and 7). Each of these variations would reduce the estimated τ (equation (9)). The conclusion must be that as the monolayer is expanded from the collapse point the timescale of the relaxation affect-ing the transverse shear modulus decreases. $\Delta\gamma_0 \sim 0$ for $\Gamma_s < 0.044$ molecules/Å^2 (figure 6): no relaxation has occurred. The relaxation time must there be substan-tially less than the inverse of ω_0 (i.e. < 1 μs), while to acount for the observed γ' values, G must be > 2.9 mN m^{-1}. If we neglect the fluctuations of $\gamma_0(\omega)$ at lower Γ_s the increase in γ' there would imply a continuation of this fall in τ, as for glycerol monoöleate [14].

These conclusions are very similar to those drawn for GMO [14], where at the collapse point a single Maxwell process characterized by $G \sim 1$ mN m^{-1} and $\tau \sim 9\ \mu s$

agreed well with the observed $\Delta\gamma_0$ and γ' data. It was hypothesized in that work that this relaxation was associated with chain melting of the acyl moieties, hindered by steric effects in a condensed monolayer. Now the fully compressed PDA monolayer is more compact than GMO (collapse area 28.5 Å^2), so the present slower relaxation fits in with this hypothesis.

Turning to the dilational modulus in this region, quantitative analysis is not easy. Both $\varepsilon_0(\omega)$ and ε' are large; indeed the dilational viscosity approaches that value where its effects upon the capillary waves saturate, so the numerical estimates shown in figure 9 may not be very reliable. Over most of this region (< 0.048 molecules/Å^2) ε obviously has been affected by relaxation, as $\varepsilon_0(\omega)$ systematically and considerably exceeds ε_0(eq). The substantial values of $\Delta\varepsilon_0$ indicate that $\tau > 1/\omega_0$, but the relaxation time cannot be estimated more precisely as it is not obvious that $\Delta\varepsilon_0$ and ε' derive from either K or S alone, nor are the very large values of ε' sufficiently well determined. The apparent agreement of $\varepsilon_0(\omega)$ and ε_0(eq) at the collapse point suggests that there either τ or G may tend to zero. Recalling that ε governs dilational modes within the monolayer, it may not be surprising that any relaxation involved should change its nature as the film becomes close-packed.

5. Conclusions

It would be tedious to reiterate the detailed conclusions reached above concerning the viscoelasticity of the various monolayer phases above and below T_t. This work, based on a data analysis procedure involving no *ad hoc* assumptions, is the first clearly to demonstrate non-zero transverse shear viscosities for monolayers of fatty acids and to show the phase dependence of the dilational viscosity. It is not possible to conclude that γ' is zero just because the capillary wave frequency and damping can be reproduced computationally for appropriate values of the other surface properties.

The monolayer behaviour below T_t provides an interesting contrast to that for $T > T_t$: a few significant points of comparison may usefully be noted. In particular, at low T both elastic and viscous parts of ε and the transverse shear viscosity γ' behave quite unexpectedly: ε_0 and ε' increase abruptly to roughly constant values at a molecular area about that of a recumbent PDA molecule, whilst γ' increases similarly at an even larger area. These variations are entirely independent and neither seems related to the classically observed condensed and gaseous phases. In the condensed phase at these low temperatures ε_0 concurs with the classical values, whereas viscoelastic relaxation of γ continues to be evident up to the collapse point. All of these aspects require further investigation. The two most notable points of the behaviour above T_t are the relaxation of the modulus ε in the LC/LE coexistence region, and the non-zero values of the transverse shear viscosity in the more expanded LE phase region. Further studies of the frequency dependence of both moduli would be useful.

In different areas of the phase diagram of pentadecanoic acid both surface viscosities have been shown to display viscoelastic relaxation. This emphasizes the dependence of the measured surface viscosities upon the timescale of the perturbations involved in their determination. Naive comparisons of high frequency light scattering values of ε' with surface shear viscosities measured with classical surface viscometers may not be very illuminating.

It is also evident that surface viscoelasticity is a very complex area of phenomenology, as illustrated by the different relaxation processes which affect the two moduli

γ and ε in different regimes. For example, in the intermediate range of surface concentration at $T < T_{\mathrm{t}}$, the modulus γ evidently relaxed rather rapidly ($\tau < 1$ μs) whereas the relaxation process affecting ε was much slower ($\tau > 50$ μs). This point is emphasized by the completely different variations of γ' and ε' with Γ_{s} for this case. However the region where γ' is non-zero for the higher T case exactly coincided with the re-emergence of ε' on expansion of the monolayer into the rather expanded LE region. Further work is required to fully understand such apparent coincidences.

A final point is that the present data emphasize the composite nature of the dilational modulus. The constituent bulk and shear moduli may be very different in magnitude and also in their relaxation processes. This may make the interpretation of any changes in ε rather difficult.

Acknowledgments

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