Universal jumps in the elastic properties of monomolecular films?

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Abstract. The dilational elastic modulus of monomolecular films at the air–water interface can be determined by surface light scattering. For two different amphiphilic molecules, n-pentadecanoic acid and glycerol monoöleate, this modulus increases discontinuously at a particular surface concentration on film compression. The magnitude of the increase, in units of $k_B T/A$, where A is the area per molecule in the film, is the same in both cases and is compatible with the value 4π. This suggests that the effect arises from the transition of the quasi-two-dimensional film from a hexatic to a solid phase.

1. Introduction

Matter in two dimensions provides continuing scientific fascination, not only as a model for three-dimensional systems, but also because of specifically two-dimensional effects. Amongst the latter are the phenomena associated with two-dimensional melting. Following the pioneering work of Kosterlitz and Thouless [1], it has been shown by Halperin and Nelson [2], and independently by Young [3], that this may involve two stages: a solid phase, with power-law decay of the positional order and long-range orientational order, melts at a temperature T_m to an intermediate phase, with exponential decay of the translational order and algebraic decay of the orientational order, which then melts at a higher temperature T_i to a normal fluid, in which both types of order decay exponentially. The intermediate phase, exhibiting exponentially decaying positional order, but algebraic decay of correlations of the bond angle, was christened 'hexatic' [2], to reflect a certain resemblance to liquid crystalline order. The body of theory involved will be referred to below as the KTHNY theory.

There have been various attempts to observe and study hexatic phases; here we confine ourselves to monomolecular amphiphilic films at the air–water interface, which provide a quasi-two-dimensional system. It is only quasi-two-dimensional because the amphiphilic molecules may possess extra degrees of orientational and conformational freedom, which potentially may inhibit KTHNY transitions. The structure of the hexatic phase is unique, permitting definite predictions of the outcome of, for example, x-ray scattering. Such studies have indeed revealed hexatic phases in monomolecular films [4].

However KTHNY theory makes other predictions that are less well supported, especially for such molecular films. In particular, the progressive unbinding of point

defects in the melting process, dislocations at T_m and disclinations at T_i, leads to predictions of dramatic changes in the elastic properties of the two-dimensional system. The Lamé coefficients approach finite limiting values as T approaches T_m from below, and just at T_m satisfy a universal relationship [2]

$$\lim_{T \to T_m^-} \left(\frac{1}{\mu(T)} + \frac{1}{\mu(T) + \lambda(T)} \right) = \frac{a_0^2}{4\pi k_B T_m} \tag{1}$$

where a_0 is the lattice spacing. The KTHNY theory thus predicts a *universal* jump in this combination of the elastic properties on melting from the solid to the hexatic phase, the magnitude of which depends on the lattice spacing in the two-dimensional material. The shear elastic modulus (μ) undergoes a finite but non-universal decrease: considerations of the two limiting cases $\lambda(T) \to 0$ and $\lambda(T) \to \infty$ shows that $\mu(T_m^-)$ must lie in the range 4π–8π in units of $k_B T_m / a_0^2$. As the system melts through T_m the shear modulus drops discontinuously from this value to zero.

For realistic perturbations the 'solid' character of the two-dimensional material persists to temperatures rather above T_m. Only for zero q do the dislocations unbind strictly at T_m; over finite length scales (finite wavelength disturbances) the dislocations interact, raising the effective melting point [5]. This effect causes the boundaries between the different two-dimensional phases to become functions of q and somewhat blurred (as sketched in figure 1). The predicted jump in elastic properties at the solid–hexatic phase boundary may thus occur at a temperature above T_m and may be somewhat more gradual than suggested above, depending on the experimental probe.
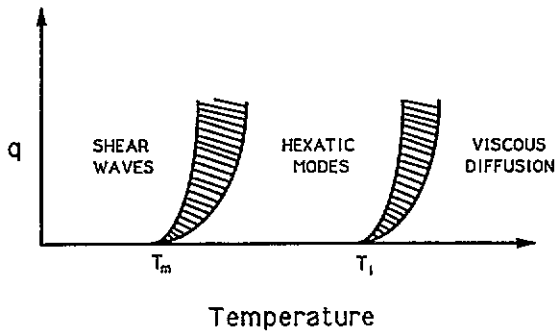

Figure 1. A sketch of the wavenumber–temperature plane for a two-dimensional system melting as predicted by KTHNY. For non-zero wavenumber the system behaves as a solid to $T > T_m$ and as a hexatic to $T > T_i$, the boundaries between the different behaviours being blurred compared to the $q \to 0$ limit (adapted from [5]).

Recent developments in x-ray technology, which have made the structural features of molecular monolayers accessible, have not been accompanied by similar advances in the determination of the elastic properties of the film. There has been one pioneering study of the Young modulus for single-solid domains of an amphiphilic monolayer [6]. We know of no investigations of monomolecular films that have established the existence of the jumps in the elastic properties predicted by KTHNY.

Light scattering by thermally excited capillary waves provides a non-perturbative method to determine the elastic properties of a molecular monolayer at the air–water

interface [7]. We consider data for two different molecular films which have been extensively studied by surface light scattering: glycerol monoöleate (GMO) [8] and *n*-pentadecanoic acid (PDA) [9]. On film compression of either PDA, at temperatures below the reported triple point (~ 17°C [10]), or GMO, a transition is observed from an expanded gaseous phase to a condensed phase. We will see that both materials display apparently universal discontinuous increases in the surface elastic properties on solidification, the magnitudes of which are in quantitative accord with the predictions of KTHNY.

2. Methods

Quasi-elastic light scattering from thermally excited capillary waves on a liquid surface provides a non-perturbative probe of the surface viscoelasticity [7]. In the presence of a molecular film the capillary (transverse) waves on the surface couple to dilational (longitudinal) modes in the film [11]. The dilational viscoelastic properties of the molecular film thus affect the propagation of the capillary waves, albeit indirectly, so that experimental studies of the latter permit the determination of these properties. The indirectness of their effects limits the precision of their determination, but this is not a great restriction in the present study.

We have used photon correlation to measure the Fourier transform of the spectrum of light scattered by capillary waves [8]. While many workers [12] have attempted to link the frequency and damping of the waves of the experimental wavenumber (q) to those surface viscoelastic properties which affect the capillary waves, the entire observed correlation function can be analyzed directly in terms of these properties [13]. The observed correlation functions are fitted with the Fourier transformed theoretical spectrum of capillary waves of the experimental q, which is a function of the relevant surface properties. This direct fitting avoids the necessity of introducing possibly inaccurate assumptions, and extracts the maximum information from the data. The principal point of present interest is that this procedure provides estimates of the surface dilational modulus ϵ.

The capillary waves impose a uniaxial dilation upon the surface monolayer, as in a standard Langmuir trough compression, so that the relevant elastic modulus is

$$\epsilon = B + \mu \tag{2}$$

where B and μ are respectively the bulk and shear moduli. It is difficult to relate ϵ directly to the Lamé coefficients of (1), as the true bulk modulus (but not the shear one) contains additional contributions arising from the creation of vacancies and interstitials [3]. The quantity ϵ is equivalent to that found from the standard surface pressure–area isotherm using $\epsilon \equiv -d\pi/d \ln A$, except that the light scattering values relate to finite q. Thus, if the film undergoes a KTHNY melting process, ϵ should increase by $\geqslant 4\pi$ (in units of $k_B T_m / a_0^2$) at the solid–hexatic transition. These predictions may be modified because of the finite-q nature of the light scattering probe of the surface dynamics.

The monolayer methods have been fully discussed elsewhere [8,9]. The surface concentration was increased by film compression by addition of successive aliquots of the film-forming solution, rather than the more usual use of a moveable barrier: the film is being solidified by compression. The succession of temperatures predicted

by KTHNY thus translates into a series of areas per molecule: T_m, T_i are replaced by A_m and A_i. In a similar way the phase transitions of two-dimensional colloidal monolayers have been studied through melting by expansion [14].

Pentadecanoic acid (> 99% purity as purchased from Fluka) was further purified before use by repeated re-crystallization from solution in pure hexane [9]. The impurity levels were sufficiently low that flat pressure–area isotherms were recorded in the first-order liquid-condensed phase transitions above the triple point of the monolayer [9]. Glycerol monoöleate (purity > 99%, Pharmacia) was used without further purification.

3. Results

We consider here data for the two amphiphiles, glycerol monoöleate [8] and *n*-pentadecanoic acid [9], the latter at temperatures below the triple point. The variations of the light scattering values of the dilational elastic modulus for these materials are shown in figures 2 and 3, together with the variations determined from the π–A isotherms. The sensitivity of light scattering to ϵ varies with the magnitude of this quantity: it is a maximum when ϵ is about 16% of the surface tension. For the dilute monolayers of present concern the tension is close to that of water ($\sim 70\,\text{mN m}^{-1}$). The data for GMO are thus expected to be quite precisely determined; those for PDA exceed the value for optimum sensitivity, although the data analysis still yields reasonably precise estimates.
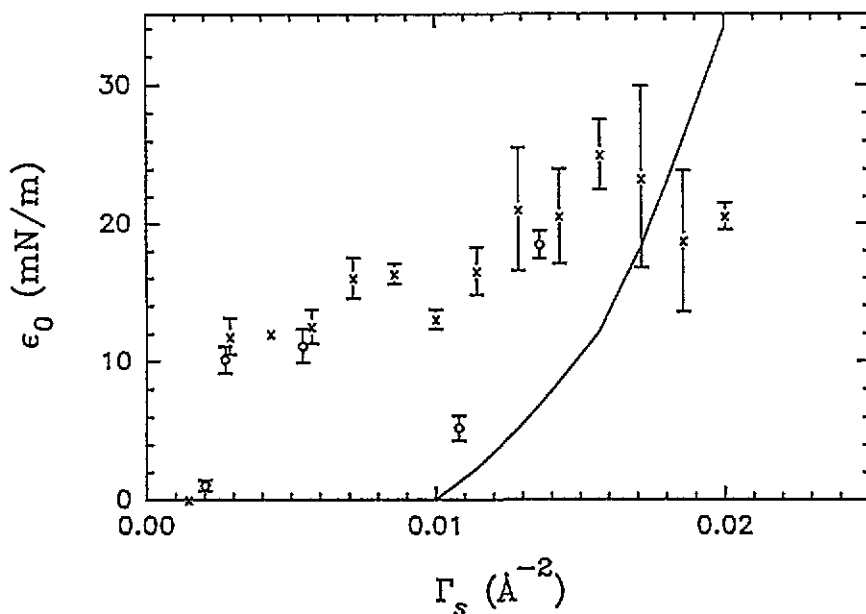

Figure 2. The dilational elastic modulus for glycerol monoöleate at 20 °C as determined by light scattering from capillary waves (o: $q = 931.9\,\text{cm}^{-1}$; x: $q = 320.6\,\text{cm}^{-1}$ [8]) and from the surface pressure–area isotherm (curve).
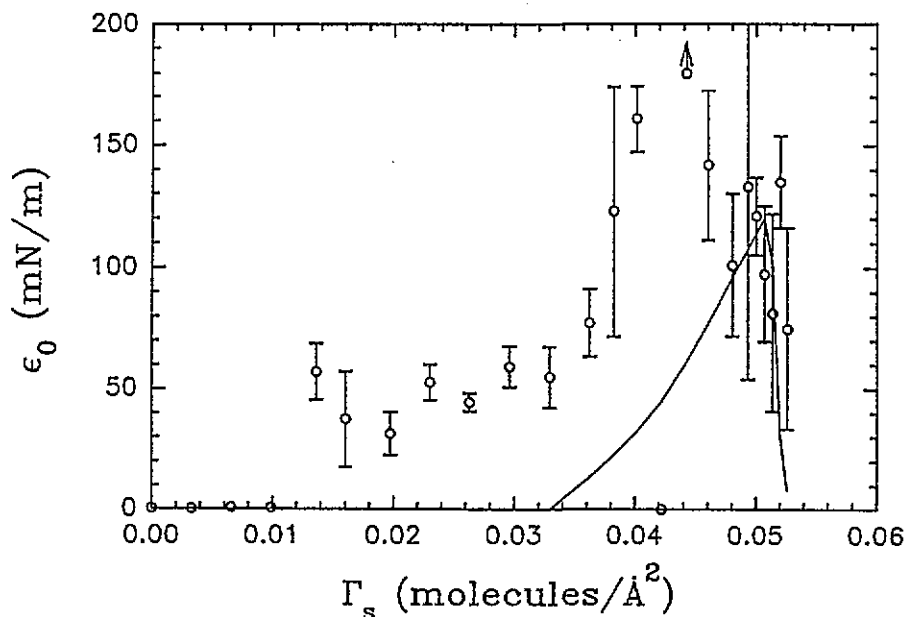
Figure 3. The dilational elastic modulus for pentadecanoic acid at 15 °C as determined by light scattering from capillary waves ($\times$: $q = 617\,\text{cm}^{-1}$ [9]) and from the surface pressure–area isotherm (curve).

At very low surface concentrations (Γ_s) the surface properties observed for GMO tended to fluctuate somewhat [8]. Recent work [15] showed that the fluctuations evident in the light scattering data ceased after a time that apparently depended upon the surface concentration. The initially inhomogeneous film eventually reaches an apparent equilibrium state, typified by the values of ϵ shown as circles in figure 2. At small surface concentrations the final value reached by ϵ was indistinguishable from that of the clean subphase (i.e. zero), whereas at somewhat larger Γ_s it assumed an essentially constant finite value. No such fluctuations were observed for PDA, presumably due to a more rapid equilibration of the surface phases. No values of ϵ intermediate between the two extremes noted above were ever observed for well equilibrated monolayers of either material.

The main feature of the data is the dramatic jump evident in ϵ for both materials. These occur at surface concentrations that differ by about five; the magnitudes of the jumps in ϵ differ by a similar factor. The data only allow the values of Γ_s corresponding to these jumps to be estimated to within more-or-less narrow limits. For PDA the jump occurs at a molecular area (A) between 73–101 Å^2, whereas for GMO the corresponding range is 370–500 Å^2. At larger surface concentrations the dilational elastic modulus ϵ appeared to be constant over a range of Γ_s, extending towards the value at which the classically determined ϵ departed from zero.

The jumps can best be discussed by considering ϵ in units of $k_B T/a_0^2$. For a_0^2 we take the centres of the ranges of A just quoted. Then, taking ϵ averaged over the range of apparent constancy at low Γ_s, ϵ is 10.3 ± 2.4 for PDA and 12.1 ± 2.8 for GMO in these units (i.e. $\epsilon a_0^2/k_B T$). Despite the different surface concentrations at which the jumps occur for the two materials the dilational elastic moduli (in units

of $k_B T / a_0^2$) are in reasonable accord. This suggests that the observed jumps may be universal. Indeed, the absolute value of the jumps seems compatible with a value 4π, in accord with KTHNY theory.

This accord with indications from KTHNY suggests that the transition from condensed to gaseous phases in these monolayers happens via a hexatic phase. The jumps in the dilational elastic modulus occur at molecular areas well above those at which the surface pressure isotherms indicate changes of phase. The precision of our surface manometry is probably not adequate to reveal any jump in the dilational modulus for $q \rightarrow 0$, as determined from the π–A isotherms (curves in figures 2 and 3). Certainly none is apparent in the data. However we note that very careful studies of the phase transition in PDA below the reported triple point [10] do seem to indicate a sharp increase in $-d\pi/d \ln A$ at the onset of the condensed phase. The present jumps in the light scattering values of ϵ occur at larger A than the lift-off of the π–A isotherms because fluctuations of finite q, such as capillary waves, involve small length scales (surface wavelengths of the order of tens of microns) over which the point defects continue to interact (being unbound only for infinite wavelength perturbations).

The data do not seem to depend markedly on q over the range used. For example, for GMO, data for $533.8\,\text{cm}^{-1}$ (not shown) agree, essentially exactly, with those at $320.6\,\text{cm}^{-1}$ [8], which also agree with those at $931.9\,\text{cm}^{-1}$ (figure 2). This lack of q dependence suggests that the experimental range of q lies above that at which the boundary between solid and hexatic phases varies (cf figure 1).

It is interesting to briefly consider the values of the dilational viscosities found from the light scattering data for the two materials. This viscosity is difficult to determine with great precision, and so the values for different molecular areas tend to fluctuate somewhat. However there do seem to be systematic differences between the two materials studied. Averaging the data over areas per molecule between 30–$73\,\text{Å}^2$, PDA yields a value of $(5 \pm 1) \times 10^{-5}\,\text{mN s m}^{-1}$ [16], while the average dilational viscosity for GMO for $88 < A < 370\,\text{Å}^2$ is $(2 \pm 1) \times 10^{-5}\,\text{mN s m}^{-1}$ [8, 15]. As for the elastic modulus, the value of the viscosity for PDA exceeds that for GMO, although the ratio is not so large as for ϵ. The viscosity of a two-dimensional solid at T_m^- is proportional to $k_B T_m / a_0^2 D$, where D is the diffusion coefficient of the molecules [5]. The values quoted would accord with this prediction if D were somewhat greater for GMO than for PDA, as would seem reasonable given that we are dealing with the more dilute monolayers in the former case. Further discussion of these dilational viscosities would seem rather speculative, in view of their large errors and some uncertainties in evaluating the theoretically predicted values.

4. Discussion

The present data suggest that the condensed-vapour phase transition in both pentadecanoic acid and glycerol monoöleate involves an intermediate hexatic phase. The large difference between molecular areas at which these two materials exhibit the jump in ϵ is somewhat surprising. The two molecules are both basically linear, about $22\,\text{Å}$ in length, and some $4\,\text{Å}$ in lateral dimension; however, the double bond in the middle of the oleate chain of GMO causes this molecule to be bent. The molecular area associated with the jump in PDA would correspond to close packing of rod-like molecules in the surface. However, the larger area for GMO roughly equals that of a

molecule rotating in the surface plane about its centre of gravity. We cannot say that this molecular picture is correct or that it underlies the difference in the A values at which the jump in ϵ occurs, but such considerations do point up the scale of the discrepancy. Despite these uncertainties, the different areas do correlate as expected with different values of the dilational elastic modulus.

It is not clear that marked structural changes should occur in the monolayers at the areas at which the jumps in ϵ are observed. For fatty acids the present low-temperature condensed phase appears to be hexatic in nature (this is the L2 phase of [4, 17]): x-ray diffraction reveals short-range positional and long-range orientational orders [18], the acyl chains being apparently tilted towards a nearest neighbour along the short side of the unit cell rectangle. However, as noted above, the solid–hexatic transition shifts to higher molecular areas (at constant T) for finite wavevector probes, due to remnant interactions of defects [5]. The molecular areas associated with the observed jumps in ϵ are thus q dependent, and the monolayer structure at these areas may not necessarily closely relate to that below A_m. We assume that some orientational order remains over distances set by $1/q$. However, our data provide no basis for hypotheses relating tilt and the transition.

Further investigations of the phenomena would be most useful, and could address such questions as the following. Do monolayers of other materials, having transitions from condensed to vapour phases, show similar effects? Does the q dependence of the phenomena (particularly A_m) follow that suggested theoretically (cf figure 1)? How do the jumps in ϵ vary with T? The latter point is particularly relevant to PDA, where the triple point at $\sim 17\,°C$ is experimentally accessible. At higher temperatures 'liquid' phases are observed in PDA [19], and effects such as those reported here are not observed. Light scattering studies in this region showed no discontinuous changes in ϵ at any temperature or molecular area studied [9]. Rather, clear first-order transitions were observed between the various phases (gaseous, liquid or liquid-expanded and solid or liquid-condensed). The present data suggest that the relevant part of the phase diagram for this material may resemble that sketched by Halperin and Nelson [2], but detailed studies are necessary. In this respect studies of various members of the homologous series of normal fatty acids may be useful. The existence of equivalent states of these different molecules [17] enables an increase in chain length to be used as an experimentally useful equivalent to an increase in temperature.

Acknowledgments

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