

# Hydrodynamics of Shape Relaxation in Viscous Langmuir Monolayer Domains

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A noncircular, liquid-condensed domain is created in liquid-expanded surroundings of a methyl octadecanoate Langmuir monolayer upon fusion of two circular domains using optical tweezers. After fusion, the relaxation to a circular shape is observed using fluorescence microscopy. The relaxation rates of the Fourier components of the shape deformation are proportional to the order of the Fourier component and in the range of  $1 \text{ s}^{-1}$ . This shows that the relaxation is dominated by the surface shear viscosity  $\eta_i = 0.41 \pm 0.1 \text{ } \mu\text{Ns/m}$  of the liquid-condensed phase.

## Introduction

Langmuir monolayers at the air/water interface exhibit peculiar patterns in phase coexistence regions.<sup>1</sup> Those patterns have successfully been described by the competition of intermolecular dipole interactions and the line tension acting at the phase boundaries. Among the patterns observed, circular domains have attracted specific attention because of their simplicity. Stability criteria<sup>2</sup> and transitions to more complicated shapes<sup>3</sup> have been observed experimentally and explained theoretically. The electrostatic interactions destabilize the circular shape of the domain. Beyond the instability, the new shape is determined by the fastest growing unstable mode of deformation, involving the hydrodynamic behavior of the Langmuir monolayer. The 2D-flow in a Langmuir monolayer is coupled to the 3D-flow of the underlying subphase. For circular domains, the surface shear viscosity of the domains  $\eta_i$ , the surface shear viscosity of the embedding matrix  $\eta_o$ , and the bulk viscosity of the subphase  $\eta_{\text{sub}}$  (see Figure 1) are generally involved. The hydrodynamics of unstable or deformed domains has been treated theoretically by Lee et al.,<sup>3</sup> by Stone and McConnell,<sup>4</sup> and by Mann et al.<sup>5</sup> Their results can be summarized as follows.

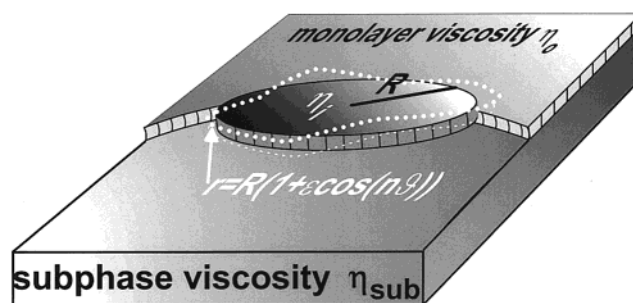
For the moment, we neglect the electrostatic interactions of the molecules inside the domain. The line tension  $\lambda$  at the phase boundary is the driving force which forces any deformed shape back to a circle. Employing polar coordinates  $r, \vartheta$  for a small deformation of the domain of radius  $R$

$$r(\vartheta, t) = R[1 + \sum_n \epsilon_n(t) \cos(n\vartheta)] \quad (1)$$

the shape will relax according to

$$\epsilon_n(t) = \epsilon_n(0)e^{-\Gamma_n t} \quad (2)$$

Here,  $\epsilon_n(t)$  are the time dependent Fourier components of the deformation of the order  $n$ , and  $\Gamma_n$  is the relaxation rate of the  $n$ th mode. If the effect of the subphase viscosity is negligible



**Figure 1.** A liquid-condensed domain of radius  $R$  and surface shear viscosity  $\eta_i$  suspended into a two-dimensional incompressible fluid (monolayer) of surface shear viscosity  $\eta_o$ . The two-dimensional fluid is coupled to a three-dimensional fluid (subphase) of viscosity  $\eta_{\text{sub}}$ . A distortion described by eq 1 (dotted line) is sketched.

( $\eta_{\text{sub}} R \ll \eta_i$  or  $\eta_o$ ), the problem can be reduced to a purely two-dimensional one, and one finds<sup>5</sup>

$$\Gamma_n = \frac{n\lambda}{2(\eta_i + \eta_o)R} \quad (3)$$

while for the case of negligible surface viscosities ( $\eta_{\text{sub}} R \gg \eta_i$  and  $\eta_o$ ), one obtains<sup>4</sup>

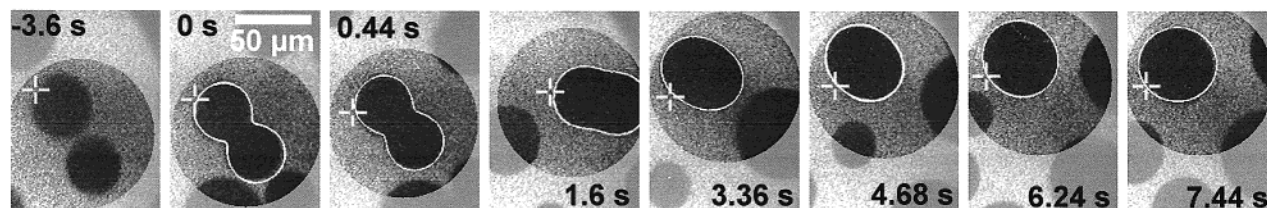
$$\Gamma_n = \frac{n^2 4(n^2 - 1)\lambda}{(4n^2 - 1)\eta_{\text{sub}} \pi R^2} \quad (4)$$

The electrostatic interactions do not effect the viscous dissipation but alter the potential energy stored in a specific shape. The only effect of electrostatic interactions is to renormalize the bare line tension  $\lambda$ . The effective line tension  $\lambda_{\text{eff}} < \lambda$  defined via

$$\lambda_{\text{eff}}[\mathbf{r}(s), \delta \mathbf{r}(s)] = \left( \frac{\delta W}{\delta P} \right)_A \quad (5)$$

is not a materials parameter. In contrast to the bare line tension  $\lambda$ , it depends on the area  $A$ , shape  $\mathbf{r}(s)$ , and the mode of

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**Figure 2.** Fluorescence microscopy images of the capture ( $t = -3.6$  s) of a domain by the tweezers (white cross) and forced fusion ( $t = 0$  s) with a neighboring domain. After fusion, the domain is rotated and translated by the tweezers while concurrently relaxing to a circular shape. Fits according to eq 10 are added as white lines. All images are taken from the same region. Regions far from the domain of interest have been shaded to draw the attention toward the captured domain.

deformation  $\delta \mathbf{r}(s)$  of the domain. Here,  $s$  denotes the arc length along the droplet and  $W$  the total energy:

$$W = (\lambda - \mu^2)P - \frac{\mu^2}{2} \oint \oint \frac{d\mathbf{s} \cdot d\mathbf{s}'}{\sqrt{(\mathbf{r} - \mathbf{r}')^2 + \Delta^2}} \quad (6)$$

The total energy  $W$  is the sum of the line energy and electrostatic energy of the droplet.  $P$  is the droplet perimeter,  $\Delta$  a cutoff length of the order of a molecular distance, and the material parameter  $\mu$

$$\mu = \sqrt{\frac{\epsilon_0}{4\pi} \frac{2\epsilon_w \epsilon_{\text{air}}}{\epsilon_w + \epsilon_{\text{air}}}} \Delta V \quad (7)$$

is proportional to the dipole density difference of the coexisting phases<sup>6</sup> and is connected with the surface potential difference  $\Delta V$  between both phases. The vacuum permittivity is denoted by  $\epsilon_0 = 8.85 \text{ pN/V}^2$  and  $\epsilon_{\text{air}}$  ( $\epsilon_w$ ) is the relative permittivity of air (water). Working out  $\lambda_{\text{eff}}$  in eq 5 with the deformation of the form (1) leads to the result<sup>3,7,8</sup>

$$\lambda_{\text{eff}}(n) = -\mu^2 \ln \frac{R}{R_n} \quad (8)$$

where

$$R_n = \frac{\Delta}{8} e^{\lambda/\mu^2} e^{Z_n} \quad (9)$$

is the radius where the circular shape gets unstable with respect to an  $n$ -fold deformation. The numbers  $Z_n$  are  $Z_2 = 7/3$ ,  $Z_3 = 8/3$ ,  $Z_4 = 73/25$ , etc. The molecular dipole interactions are taken into account by replacing the bare line tension  $\lambda$  in eqs 3 and 4 by the effective line tension  $\lambda_{\text{eff}}$  in eqs 8 and 9. The effective line tension  $\lambda_{\text{eff}}$  reduces the decay rates  $\Gamma_n$  and changes the relative amplitude ratio  $\Gamma_n/\Gamma_m$  of two-harmonic modes  $n$  and  $m$ . If, for example, the surface shear viscosity of the domain is large, one would expect that because of the mode dependency of  $\lambda_{\text{eff}}$ , the ratio of the rates  $\Gamma_n/\Gamma_m$  should deviate from  $n/m$ .

Shape relaxations have been studied by Lee et al.,<sup>3</sup> Mann et al.,<sup>5</sup> and Benvegnu et al.<sup>9</sup> All experiments were carried out under conditions where the subphase viscosity  $\eta_{\text{sub}}$  dominates the flow pattern.

In the present study, we focus on the limit of purely two-dimensional flow and show the validity of eq 3. With a combination of optical tweezers and fluorescence microscopy,<sup>10</sup> we simultaneously manipulate and visualize a Langmuir monolayer of methyl octadecanoate. Two liquid-condensed  $L_2$  domains are fused by pushing them together with a silica sphere immersed in the monolayer and trapped in the moving tweezers. The resulting single domain possesses a strongly deformed shape. The relaxation of this shape is analyzed. We show that

the viscosity of the liquid-condensed domain dominates the relaxation process. Electrostatic effects amount for a reduction of the line tension and the relaxation rates by approximately 30%.

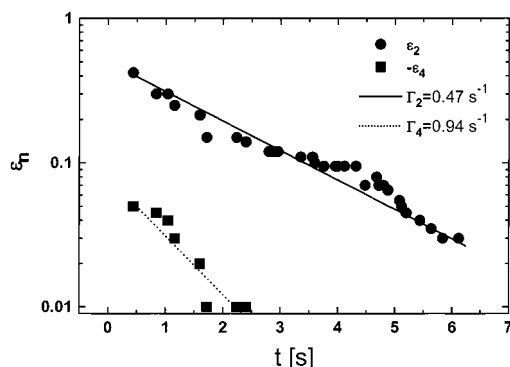
## Results

The experiments are performed in methyl octadecanoate in the coexistence region liquid condensed (LC)/liquid expanded (LE) at a temperature of  $\vartheta = 35^\circ \text{C}$  on pure water ( $\eta_{\text{sub}} = 0.725 \text{ mNs/m}^2$ ). Silica beads [Bangs Laboratories,  $\varnothing = 4.8 \mu\text{m}$ ] are immersed into the monolayer by spreading from a chloroform suspension. They absorb at the LC/LE boundaries via dipole–dipole interaction.<sup>11</sup> Using galvano scanner mirrors, the focus of the tweezers can be moved laterally in the interface. In the experiments, we used a sinusoidal movement of the tweezers  $y(t) = y_0 \sin(\omega t)$  with  $y_0 = 6.5 \mu\text{m}$  and  $\omega = 16 \text{ s}^{-1}$ .

In Figure 2, a bead attached to a domain of radius  $R = 21.4 \mu\text{m}$  is captured ( $t = -3.6$  s) by the tweezers (white cross) and forced to follow the motion imposed by the tweezers. After being pushed onto a neighboring domain of radius  $R = 19.1 \mu\text{m}$ , both domains are fused ( $t = 0$  s). After the fusion, we could not switch off the tweezers' motion fast enough so the motion of the tweezers continues, thereby translating and rotating the newly formed domain ( $t = 0$ – $7.44$  s), while its shape relaxes to a circle. Translation and rotation of the domain are governed by the viscous drag of the subphase.<sup>12</sup> As we will show, the surface shear viscosity of the domain is much larger than that of the surrounding LE phase and larger than that of  $\eta_{\text{sub}}R$ . Therefore, the translational and rotational motion, which is determined by the viscous drag of the subphase, decouples from the shape relaxation, which is dominated by the domain internal flow. The motion of the tweezers introduces no new complications for the shape hydrodynamics. We have fitted the shape with

$$|\mathbf{r} - \mathbf{r}_{\text{center}}|(\vartheta, t) = R\{1 + \epsilon_2(t)\cos[2(\vartheta - \varphi(t))] + \epsilon_4(t)\cos[4(\vartheta - \varphi(t))]\} \quad (10)$$

where  $\mathbf{r}_{\text{center}}$  and  $\varphi(t)$  describe the domain translation and rotation,  $R = 27 \mu\text{m}$ , and the parameters  $\epsilon_n(t)$  are the same as defined in eq 1. The fits are added to Figure 2 with white lines surrounding the domain under study. Because of the symmetry of the deformation, no odd Fourier components were needed. Figure 3 shows a plot of  $\epsilon_2$  and  $-\epsilon_4$  as a function of time  $t$ . Both Fourier components decay exponentially as predicted by eq 3 and 4 with rates  $\Gamma_2 = 0.47 \pm 0.02 \text{ s}^{-1}$  and  $\Gamma_4 = 0.94 \pm 0.5 \text{ s}^{-1}$ . Wurlitzer et al.<sup>13</sup> have determined the bare line tension  $\lambda = 7.5 \pm 1 \text{ pN}$ , and Heinig et al.<sup>14</sup> have determined the surface potential difference  $\Delta V = 0.38 \pm 0.02 \text{ V}$ , hence  $\mu^2 = 0.2 \text{ pN}$ . We calculate, using  $\Delta = 1 \text{ nm}$ , that the effective line tensions  $\lambda_{\text{eff}}(n=2) = 5.22 \pm 1 \text{ pN}$  and  $\lambda_{\text{eff}}(n=4) = 5.26 \pm 1 \text{ pN}$  of both modes are essentially the same and reduced by ap-



**Figure 3.** Plot of the second and fourth Fourier coefficient  $\epsilon_2$  and  $-\epsilon_4$  vs time. Both decays follow an exponential behavior with  $\Gamma_2 = 0.47 \pm 0.02 \text{ s}^{-1}$  and  $\Gamma_4 = 0.94 \pm 0.5 \text{ s}^{-1}$ , proving the dominance of the surface shear viscosity of the LC phase in the relaxation process.

proximately 30% compared to the bare line tension. The surface shear viscosity of the LE phase is negligible<sup>12</sup> for the shape relaxation, and using eq 3, we find with either deformation mode  $\eta_i = 0.41 \pm 0.1 \text{ } \mu\text{Ns/m}$ . The experimentally determined ratio  $\Gamma_2/\Gamma_4$  fulfills  $\Gamma_2/\Gamma_4 = 2/4 \pm 0.1$  as required by eq 3, and the ratio  $\eta_i/R\eta_{\text{sub}} \approx 20$  is larger than 1, justifying the use of eq 3. Equation 4 would lead to inconsistent results as one should find  $\Gamma_2/\Gamma_4 = 0.21$ , and one also had to assume an effective line tension much smaller as found in ref 13. The results also show that the hexatic LC phase behaves like a 2D-Newtonian liquid. Non-Newtonian behavior, as observed by Kurnaz and Schwartz<sup>15</sup> and by Ivanova et al.,<sup>16</sup> at comparable shear rates and surface shear viscosities in fatty acids would result in relations differing from eq 3. None of the sort has been observed in methyl octadecanoate.

### Conclusions

The correspondence between the experiments and the theoretical calculation confirms the hydrodynamic model of shape

relaxations of viscous Langmuir monolayer domains.<sup>4,5</sup> Hexatic LC domains of methyl octadecanoate behave like isolated droplets of a 2D-Newtonian viscous fluid of surface shear viscosity  $\eta_i = 0.4 \text{ } \mu\text{Ns/m}$ . Electrostatic intermolecular dipole interaction reduces the LC/LE line tension and the relaxation rates of shape deformations by 30% but has little effect on the relative ratio of the relaxation rates of the different modes.

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