Swelling kinetics of a compressed lamellar phase

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Abstract. We investigate how multilamellar vesicles prepared in a compressed state under flow return to equilibrium. The kinetics is studied by following the temporal evolution of the viscoelasticity after the shear is stopped. It exhibits a two-step relaxation whose slower stage is strongly affected by temperature. According to a simple model, the temperature-dependent permeability of the lamellar phase is deduced from the measurements. We propose to attribute the permeability to handle-like defects, and its temperature dependence to an increase of the defect density when the lamellar-to-sponge phase transition is approached.

PACS. 05.70.Ln Nonequilibrium and irreversible thermodynamics – 61.30.Jf Defects in liquid crystals – 83.70.Hq Heterogeneous liquids: suspensions, dispersions, emulsions, pastes, slurries, foams, block copolymers, etc.

1 Introduction

It has been recently shown that the effect of shear on lyotropic lamellar ($L_\alpha$) phases can be described using an orientation diagram [1]. As a generalisation of equilibrium phase diagrams, the orientation diagram maps the shear-induced (steady) textures as a function of a dynamic parameter—usually the shear rate—and a thermodynamic parameter—e.g., the volume fraction of membranes. By increasing the shear rate, one commonly encounters three steady states: at very low shear rate (typically $\dot{\gamma} < 1$ s$^{-1}$, depending on concentration) a partially oriented state with the normal to the smectic layers parallel to the shear gradient; at intermediate shear rates ($1 < \dot{\gamma} < 500$ s$^{-1}$), the membranes roll up onto themselves to form multilamellar, monodisperse and close-packed vesicles—the so-called onion texture; at even higher shear rates, one gets back-oriented membranes. These various organisations are separated by dynamic transitions which were characterised using rheology [2,3]. It is important to note that although quite general [4,5], this behaviour is not universal and remains very system-dependent [6–8]. Moreover, the mechanism of onions formation is still under a theoretical debate [9,10].

The onion texture is fascinating in many aspects. For instance, it offers a unique way to control perfectly the texture of the lamellar phase on macroscopic scales. Typically of order of 1 $\mu$m, the size of the multilamellar vesicles is fixed by the shear rate and follows a power law ($R \sim \dot{\gamma}^{-1/2}$) as measured by small-angle light scattering [1] (this power law appears to be somewhat system-dependent). Some characteristics of the vesicular state on properties of $L_\alpha$ phases were given using conductivity [11] and viscoelasticity [12].

Recently, the opportunity to control additionally the spatial organisation of the onions was demonstrated [13–15]. Indeed, for one particular $L_\alpha$ phase a series of dynamic transitions leads to a population of shear-ordered onions, in a close analogy with the shear ordering of concentrated colloidal suspensions [16]. The resultant texture consists of hexagonal planes of onions sliding on each other under flow and referred to as the layered state of onions.

In this article, we focus our attention on a very peculiar onion regime where the vesicles are nonetheless well ordered but also compressed under flow. This state is evidenced by combining several experimental observations (light scattering, neutron scattering, etc.) and consists of large multilamellar vesicles which, under flow, have expelled some of their inner water. We use this opportunity to investigate the relaxation processes of the compressed vesicles once the shear is stopped. Studied by means of viscoelasticity, the kinetics exhibits a two-step process: whereas the first stage is relatively fast ($\tau \approx 100$ s) and, as a consequence not well resolved using rheology alone, the second stage is much slower ($\tau \approx 0.5–3$ hours). It is also strongly dependent upon the working temperature. We attribute this second stage to the swelling of the vesicles by the expelled water. According to a simple diffusion model for the membrane displacement, we deduce from the slow kinetics the permeability of the lamellar phase. We find that it strongly increases when temperature is raised. We
propose to correlate this last effect to the proliferation, close to the lamellar-to-sponge phase transition, of handle-like defects [11] connecting the membranes.

2 The state of compressed onions

The \( L_\alpha \) phase we studied is a quaternary mixture of sodium-dodecyl sulfate, octanol and brine (7%, 8%, 85% w/w, respectively, NaCl at 20 g/l) whose phase diagram has already been published [17]. This \( L_\alpha \) phase is stabilised by steric interactions [18] and its smectic period is \( d \approx 160 \, \text{Å} \) for this composition. At equilibrium, the system undergoes a lamellar-to-sponge phase transition when the temperature is raised around \( T \approx 31^\circ \text{C} \).

The orientation diagram was studied in the plane \((T, \dot{\gamma})\) [14,19]. One distinguishes two regimes depending on the temperature. At low temperature \((T < 26^\circ \text{C})\), the sequence of membrane organisations is the following: at very low shear rate \((\dot{\gamma} < 1 \, \text{s}^{-1})\), the membranes are preferentially oriented in the direction of the flow; at a first critical shear rate \((\dot{\gamma} \approx 1 \, \text{s}^{-1})\), the phase undergoes the lamellar-to-onion transition; above a second critical shear rate \((\dot{\gamma} \approx 50 \, \text{s}^{-1})\), the onions get spontaneously ordered \((\text{layered onions})\). The transition only reorganizes the spatial locations of the onions from an amorphous \((\text{the local order that does not extend further than typically the third neighbour})\) to a more ordered state, without any change in the onion size. Finally, one retrieves oriented membranes above a third critical shear rate \((\text{note, however, that the shear values at the transition depend on } T [14, 19])\). At high temperature \((26 < T < 31^\circ \text{C})\), the sequence is analogous, apart from the high shear rate regime. Instead of oriented membranes, a new transition takes place \((\text{the jump-of-size transition})\) whose main features are the following:

1) at the transition the size of the onions increases discontinuously from 1 to 10 \( \mu \text{m} \) typically and then does not depend any more on the shear rate [14];
2) the transition is accompanied with a decrease of the smectic period of the lamellar phase [13].

The second point is shown in Figure 1(a) where we display the modification of the small-angle neutron scattering (SANS) profiles (spectrometer PAXY, Laboratoire Léon-Brillouin, laboratoire commun CEA-CNRS, Saclay, France) under shear, below and above the jump-of-size transition. Below the transition, there is no noticeable effect of shear on the SANS profile. Above the transition, the Bragg peak of the smectic stacking is shifted towards higher wave vectors than the equilibrium one, which corresponds to smaller smectic distances. The systematic study as a function of the shear rate leads to Figure 1(b) where we see that \( d \) decreases continuously with \( \dot{\gamma} \) above the jump-of-size transition. Meanwhile, the numerous Bragg spots of the small-angle light scattering patterns [13] not only show that the onions still exist but also that they are extremely well ordered under shear.

The combination of these results (light+neutron scattering) suggests that the onions have expelled some of the inner water and subsequently this state will be referred to as compressed onions. While not proven, it was argued in reference [13] that the shear rate—usually fixing the size of the vesicles (through a mechanism where the viscous stress is balanced against the energetical cost of making a vesicle [1])—now acts as a compression force. This could be the reason why the size of the vesicles does not depend anymore on the shear rate and, instead, the shear rate controls the compression.

It is also possible to evidence this compressed state using macroscopic techniques instead of small-angle neutron scattering. Let us first recall that at least two paths of the orientation diagram may lead to the compressed state of onions. For instance, one can either work at constant