



# Macroscopic dynamics near the isotropic micellar to lamellar phase transition



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## ABSTRACT

We present the hydrodynamic equations for the lamellar phase in lyotropic liquid crystals. The hydrodynamic equations are investigated to the vicinity of the isotropic micellar to lamellar phase transition. To derive the hydrodynamic equations we make use of symmetry arguments and irreversible thermodynamics. Besides the usual order parameters to describe the lamellar phase we also keep the concentration of the surfactant molecules which are aggregated in micelles as a variable in order to describe the correct macroscopic behavior of the lamellar phase. The macroscopic dynamic equations are presented on both sides of the transition. We discuss possible experiment were our theory can be tested.

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## 1. Introduction

Lyotropic liquid crystals (LLC) are mixtures of amphiphilic molecules and solvents at given temperature and relative concentrations. An important feature of LLC is the self-assembly of the amphiphilic molecules as supermolecular structures. Lyotropic mesophases are very similar to the mesophases that exist in thermotropic liquid crystals (TLC) in terms of the orientational and translational ordering. Smectic-A (SmA) phase in TLC is composed of parallel liquid layers. In general the lamellar phase is a SmA liquid crystal in which the layers are composed of surfactants molecules and the gap between them is occupied by water. This phase is designated as  $L_D$ . Thus the  $L_D$  phase exhibits the positional ordering of micelles into planes arranged periodically along the nematic director  $\hat{n}$ . In many systems, such as lyotropic liquid crystals [1–4] and block copolymers [5–10] transition is observed from a uniform isotropic to a lamellar phase upon lowering the temperature. Alexandridis et al. [9] studied the phase behavior and structure of binary amphiphilic polymer-water systems as a function of polymer concentration and temperature for three poly (ethylene oxide)-b-poly (propylene oxide)- b-poly (ethylene oxide) (PEO-PPO-PEO) copolymers of different composition by using 2H-NMR and small-angle X-ray scattering. They observed three different cubic, hexagonal, and lamellar LLC phases. The characteristic lattice parameter of the lamellar structure decreased with increasing polymer content; the bilayers swell less as water is removed. Wanka et al. [10] also studied the phase diagrams and aggregation

behavior of triblock copolymers in aqueous solutions. They also confirmed three different cubic, hexagonal, and lamellar LLC phases. Experimental results [1–4] and theoretical predictions [11–14] support the evidence of the presence of a transition from the isotropic micellar (I) to a lamellar phase transition in LLC system. In experimental studies [1–4], the binary mixtures of cesium perfluoro-octanoate (CsPFO)-water/heavy water ( $H_2O/D_2O$ ) and APFO/ $D_2O$  systems were found to produce the I,  $N_D$  and  $L_D$  phases and the I- $L_D$  transition via a I -  $N_D$  -  $L_D$  triple point. The I- $L_D$  phase transition is quite analogous to the isotropic-smectic-A (I-SmA) phase transition in TLC. Experimentally I- $L_D$  phase transition is found to be strongly first order. In a recent paper [14], we theoretically studied the key features of the I- $L_D$  phase transition in detail. It was pointed out that the same pretransitional behavior occurs for the I- $L_D$  phase transition similar to the I-SmA transition in TLC. The purpose of the present paper is to study the hydrodynamic properties near the I- $L_D$  phase transition.

Liquid crystalline phases have interesting hydrodynamic properties which is known for over four decades both in TLC [15–23] and LLC [24–28]. It turns out that the anisotropy of TLC has a number of interesting implications for their hydrodynamic behavior. The macroscopic dynamics deal with the dynamics of the deviations of the order parameter modulus from its equilibrium value. It is valid only near the phase transition. Although the hydrodynamic and macroscopic dynamics study in TLC have been a topic of active theoretical and experimental studies over the four decades, reports of the macroscopic dynamics study in LLC are comparatively scarce. It is the goal of this paper to study the macroscopic dynamics behavior near the I- $L_D$  phase transition. Brochard and de Gennes [24] extensively studied the hydrodynamic

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properties of fluid lamellar phases of lipid/water system. The observations of the collective modes in the lamellar phases shows details of the interactions between layers and also on specific dissipative process in the lipid region. Bary-Soroker and Diamant [28] studied the relaxation modes of an interface between a lyotropic lamellar phase and a gas or a simple liquid. They found that surfaces of lyotropic lamellar phases can relax via a much slower, over-damped diffusive mode over a wide range of wavelengths.

To the best of the author knowledge there is so far no theoretical work on the macroscopic dynamics study near the I- $L_D$  phase transition. Thus it is interesting to study the macroscopic dynamics behavior near the I- $L_D$  phase transition. In the present paper we study the macroscopic dynamic behavior near I- $L_D$  phase transition. We adopt the general framework developed by us in our previous work [29] for the isotropic to Smectic-A (I-SmA) phase transition in TLC and for dynamics of binary liquid crystal mixtures [23,30,31]. We identify different hydrodynamic and macroscopic dynamic variables near the I- $L_D$  phase transition.

## 2. Derivation of macroscopic equations

### 2.1. Macroscopic equations in the $L_D$ phase below the I- $L_D$ transition

We start by describing the hydrodynamic and macroscopic variables in the  $L_D$  phase that describes the macroscopic state of the system. The hydrodynamic variables for the lamellar phase are density  $\rho$ , entropy density  $\sigma$ , density of linear momentum  $\mathbf{g}$ , displacement  $u_z$  of the smectic layers along the  $z$  axis associated with the density wave parallel to the layer normal and  $\phi$  which measures the concentration of those surfactant molecules which are aggregated in micelles. Here  $\phi = (x - x_i)$ , where  $x_i$  is the molar fraction of the free surfactant molecules and  $x$  is the total molar fraction of the surfactant. Here  $x = n_{sr}/(n_{sr} + n_s)$ , where  $n_{sr}$  and  $n_s$  denote the numbers of surfactant and solvent molecules, respectively. The  $L_D$  phase has the same symmetries as the smectic-A (SmA) phase in TLC. So the macroscopic variables for the  $L_D$  phase are the modulus  $S$  of the nematic order parameter  $Q_{ij} = (S/2)(3n_i n_j - \delta_{ij})$ , the real modulus of the smectic order parameter  $W$  similar to SmA phase in TLC. We also assume that the nematic director  $\hat{\mathbf{n}}$  and the smectic layer normal  $\hat{\mathbf{k}}$  are parallel to each other. Here we will focus only on the linearized macroscopic equations. To describe the static properties of the  $L_D$  phase, we find the Gibbs relation in terms of the hydrodynamics and macroscopic variables

$$d\varepsilon = \mu d\rho + T d\sigma + v_i g_i + \Psi_i d\nabla_i u_z + N d\phi + P dS + M dW \quad (2.1)$$

where  $\varepsilon$  is the energy density. In Eq. (2.1) the thermodynamic quantities chemical potential ( $\mu$ ), temperature ( $T$ ), the velocity field  $v_i$ , the field  $\Psi_i$ , the concentration field  $N$  and the order parameter fields  $S$  and  $W$  are defined as partial derivatives of the thermodynamic potential with respect to the appropriate variables.  $N$  is a conjugate quantity of  $\phi$ . So  $N$  is analogous to relative chemical potential  $\mu_\phi$ . Equation (2.1) gives a relation between the changes in the macroscopic variables and the entropy density  $\sigma$ .

Now the generalized energy ( $F = F_0 + \int f d\tau$ ) of the lamellar phase can be written as

$$F = F_0 + \int d\tau \left[ \frac{1}{2} a S^2 + (b^\rho \delta\rho + b^\sigma \delta\sigma) S + \frac{1}{2} \alpha W^2 + (c^\rho \delta\rho + c^\sigma \delta\sigma) W + \frac{1}{2} p_1 (\delta\phi)^2 + (f^\rho \delta\rho + f^\sigma \delta\sigma) \delta\phi + h S W + k S \delta\phi + m W \delta\phi + \frac{1}{2} B (\nabla_z u_z)^2 + \frac{1}{2} K (\nabla_\perp^2 u_z)^2 + (d^\rho \delta\rho + d^\sigma \delta\sigma + d^W W) \nabla_z u_z + \gamma_1 (\nabla_z u_z) S + \gamma_2 (\nabla_z u_z) \delta\phi \right], \quad (2.2)$$

where  $F_0 = \int f_0 d\tau$  is generalized energy of the isotropic liquids with  $f_0 = \int \left[ \frac{1}{2} A_{\rho\rho} (\delta\rho)^2 + A_{\rho\sigma} (\delta\rho)(\delta\sigma) + \frac{1}{2} A_{\sigma\sigma} (\delta\sigma)^2 + \frac{1}{2\rho} g^2 \right]$ , where  $A_{\rho\rho} = (\partial\mu/\partial\rho)_\sigma$ ,  $A_{\rho\sigma} = (\partial T/\partial\rho)_\sigma$ , and  $A_{\sigma\sigma} = (\partial T/\partial\sigma)_\rho$ . Here  $B$  is the compressional modulus of the smectic layers and the layer bending modulus  $K$  is close in magnitude to the splay modulus in nematic. The transverse Laplacian is defined as  $\nabla_\perp^2 = (\delta_{ij} - n_i n_j) \nabla_i \nabla_j$ .

Now the conjugated variables in terms of the hydrodynamic and macroscopic variables are expressed as

$$P = \frac{\delta F}{\delta S} = a S + b^\rho \delta\rho + b^\sigma \delta\sigma + h W + k \delta\phi + \gamma_1 \nabla_z u_z, \quad (2.3)$$

$$M = \frac{\delta F}{\delta W} = \alpha W + c^\rho \delta\rho + c^\sigma \delta\sigma + h S + m \delta\phi + d^W \nabla_z u_z, \quad (2.4)$$

$$\Psi_i = \frac{\delta F}{\delta (\nabla_i u_z)} = (B \nabla_z u + d^\rho \delta\rho + d^\sigma \delta\sigma + d^W W + \gamma_1 S + \gamma_2 \delta\phi) \delta_{iz} - K (\delta_{ij} - n_i n_j) \nabla_j \nabla_\perp^2 u_z, \quad (2.5)$$

$$N = \frac{\delta F}{\delta (\delta\phi)} = p_1 \delta\phi + f^\rho \delta\rho + f^\sigma \delta\sigma + k S + m W + \gamma_2 \nabla_z u_z, \quad (2.6)$$

$$\delta T = \frac{\delta F}{\delta \sigma} = A_{\sigma\sigma} \delta\sigma + A_{\rho\sigma} \delta\rho + b^\sigma S + c^\sigma W + f^\sigma \delta\phi + d^\sigma \nabla_z u_z, \quad (2.7)$$

$$\delta\mu = \frac{\delta F}{\delta \rho} = A_{\rho\rho} \delta\rho + A_{\rho\sigma} \delta\sigma + b^\rho S + c^\rho W + f^\rho \delta\phi + d^\rho \nabla_z u_z, \quad (2.8)$$

$$v_i = \frac{1}{\rho} g_i. \quad (2.9)$$

To determine the dynamics of the variables we have two class of variables (1) the variables that contains conserved quantities and (2) the variables that contains nonconserved quantities.

Then the resulting dynamic equations for the conserved fields are

$$\frac{\partial \rho}{\partial t} + \nabla_i g_i = 0, \quad (2.10)$$

$$\frac{\partial g_i}{\partial t} + \nabla_j \sigma_{ij} = 0. \quad (2.11)$$

$$\frac{\partial \phi}{\partial t} + v_i \nabla_i \phi + \nabla_j j_i^\phi = 0 \quad (2.12)$$

where  $\sigma_{ij}$  is the stress tensor and  $j_i^\phi$  is the concentration current.

There is also another mass conservation equation for the  $L_D$  phase appears because of the surfactant migration in the layers plane relative to water i.e. of slip. As Brochard and de Gennes [24] pointed out that there is a constraint relation between  $\phi$ ,  $\frac{\partial u}{\partial z}$  and the relative variation of the surface per polar head ( $\delta$ ) i.e.  $\phi = \frac{\partial u}{\partial z} + \delta$ . Then the mass conservation equation due to slipping is given by Brochard and de Gennes [24]

$$\frac{\partial \phi}{\partial t} + \nabla_i v_{iL} = 0, \quad (2.13)$$

where  $v_{iL}$  is velocity of the lipid fraction and  $\frac{\partial \phi}{\partial t} = \frac{\partial (\frac{\partial u}{\partial z})}{\partial t} + \frac{\partial \delta}{\partial t}$ .

We will now write down the boundary conditions for Eqs. (2.10) and (2.11). At the interface, the differential form of dynamic Eqs. (2.10) and (2.11) are not valid anymore. Adopting the procedure as outlined by Bary-Soroker et al. [28,32], we consider an elementary box in the interface. Then at the interface Eq. (2.10) can be written as

$$\frac{d}{dt} \int_V \rho dV = - \int_S \mathbf{g} \cdot \hat{\mathbf{n}} dS. \quad (2.14)$$

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