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# PHASE SEPARATION IN LIQUID CRYSTAL/GEL COMPOSITES: ROLE OF NETWORK ELASTICITY

Nariya Uchida [a]

[a] Department of Physics, Kyoto University, Kyoto, 606, Japan

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# Phase Separation in Liquid Crystal/Gel Composites: Role of Network Elasticity

NARIYA UCHIDA

*Department of Physics, Kyoto University, Kyoto 606, Japan*

Phase separation in gels swollen by nematic solvents is investigated using a time-dependent Ginzburg-Landau model. We demonstrate that elasticity of the polymer network is responsible for a foam-like domain morphology observed in polymer dispersed liquid crystals (PDLCs). Rubber elasticity also prevents domain merger, leading to a coarsening behavior substantially slower than in liquid-liquid demixing. We briefly discuss phase separation in nematic polymer gels, in which operates a novel anchoring mechanism mediated by elastic strain.

*Keywords:* nematics; polymer networks; phase separation; PDLC

## INTRODUCTION

Liquid crystals and gels can be combined to form various composite materials, which have been extensively studied in recent years[1,2]. A representative example is the polymer dispersed liquid crystal (PDLC), a material originally developed for use in electro-optical devices. PDLCs are processed by phase separation of liquid crystal/polymer mixtures, accompanied by a chemical crosslinking (for polymerization-induced phase separation, PIPS) or a glass transition (for thermally-induced phase separation, TIPS) of the polymers. In both cases, the final product is a dispersion of liquid crystal droplets confined in a rubbery polymer matrix. Recent experimental studies

have characterized the kinetics of phase separation[3] and resulting morphology[4,5,6] from physical points of view. They suggest that elasticity of the matrix plays an important role in determining the droplet morphology, which is foam-like (polyhedral) or spherical depending on the polymer's volume fraction. On the other hand, theoretical attempts to model the fabrication process of PDLCs have been rather scarce[7,8,9]. Teixeira and Mulder[7] gave a phenomenological Ginzburg-Landau description of gelation and/or glass transition. Chiu and Kyu[8] modeled a PDLC as a rod/polymer solution to simulate the phase separation kinetics. These models neglect rubber-like elasticity. Lee[9] has recently conducted a molecular dynamics study of phase separation accompanied by polymerization. His model takes elastic and hydrodynamic effects into account while it neglects liquid-crystalline nature of the solvent. In this article, we present a minimal Ginzburg-Landau model that accounts for both elasticity of the polymer network and anisotropy of the solvent. We do not consider polymerization kinetics and model a PDLC as a gel swollen by a nematic solvent. Hence our model is applicable mainly to late stages of the phase separation (However, according to Serbutoviez *et al.*[6], there are cases where polymerization and gelation are completed before phase separation sets in. In such cases our model is applicable to the whole process of phase separation.) We also briefly discuss phase separation in gels made up of nematic polymers.

## GINZBURG-LANDAU MODEL

In this section we construct a Ginzburg-Landau model of a gel swollen by a solvent consisting of rod-like molecules. The basic variables of the model are the tensorial nematic order parameter $\mathsf{Q} = \mathsf{Q}(\boldsymbol{r})$ of the solvent and the elastic displacement $\boldsymbol{u} = \boldsymbol{u}(\boldsymbol{r})$ of the polymer network. The polymer volume fraction $\phi = \phi(\boldsymbol{r})$ is not an independent variable and expressed in terms of $\boldsymbol{u}$, as we explain below. The free energy $F$ consists of four parts as $H \equiv Fv_0/k_BT = H_{FH} + H_L + H_F + H_{el} + H_{int}$, where $v_0$ is the monomer volume and $H_{FH}$, $H_{el}$, $H_L$, and $H_{int}$ are respectively the Flory-Huggins, rubber-elastic, Landau-de Gennes, and interfacial contributions.

The mixing free energy of a gel is written as

$$H_{FH} = \int d\boldsymbol{r}\left[\frac{1}{N_s}(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right], \tag{1}$$

where $N_s$ is the volume of a solvent molecule measured in the unit $v_0$. The classical affine-deformation theory of rubber elasticity prescribes a free energy of the form[10]

$$H_{el} = \int d\boldsymbol{r}\frac{\phi}{2N}\left[\mathrm{Tr}\,\Lambda\cdot\Lambda^{\mathrm{T}} + \ln\frac{\phi}{\phi_0}\right], \tag{2}$$

where $N$ is the number of monomers per subchain, $\Lambda$ is the deformation tensor and $\phi_0$ is the polymer volume fraction at the moment of crosslinking. The deformation tensor is defined as

$$\Lambda_{ij} = \frac{\partial r_i}{\partial r_j^0}, \tag{3}$$

where $\boldsymbol{r}_0 = \boldsymbol{r}_0(\boldsymbol{r}) = \boldsymbol{r} - \boldsymbol{u}(\boldsymbol{r})$ is the initial position of the material element that is currently located at $\boldsymbol{r}$. The polymer volume fraction $\phi$ is related to its initial value $\phi_0$ as

$$\phi = \frac{\phi_0}{\det\Lambda}. \tag{4}$$

The field of elastic force acting on the network, which we denote by $\boldsymbol{g}$, is given by

$$\boldsymbol{g} = -(\mathrm{I} - \nabla\boldsymbol{u})\cdot\frac{\delta F}{\delta\boldsymbol{u}}, \tag{5}$$

where the extra factor $\mathrm{I}-\nabla\boldsymbol{u} = \partial\boldsymbol{r}_0/\partial\boldsymbol{r}$ accounts for a transformation from the comoving to stationary coordinate system.

For a 2D system, the Landau-de Gennes free energy up to the fourth order reads

$$H_L = \int d\boldsymbol{r}\left[\frac{A(\phi)}{2}\mathrm{Tr}\,\mathrm{Q}^2 + \frac{C(\phi)}{4}(\mathrm{Tr}\,\mathrm{Q}^2)^2 + \frac{L(\phi)}{2}(\nabla\mathrm{Q})^2\right]. \tag{6}$$

We have determined the coefficients $A(\phi)$ and $C(\phi)$ by a mapping from the Maier-Saupe potential, which is outlined in Appendix. Accordingly, the functions $A(\phi)$ and $C(\phi)$ are specified by three molecular parameters, viz., $N$, $N_s$, and the nematic interaction parameter

$w$. The Frank elastic coefficient $L(\phi)$ is assumed constant and left as a phenomenological parameter. We model the interfacial free energy in the form

$$F = \int d\boldsymbol{r} \frac{1}{2}(M_0 + M_1 \mathrm{Q}) : (\nabla\phi)(\nabla\phi), \tag{7}$$

where $M_0$ and $M_1$ are constants. For a sharp interface lying in the $x$-$y$ plane, the term containing $M_1$ reduces to the Rapini-Papoular form of the anchoring potential $\int\int dxdy(W/2)(\boldsymbol{n} \cdot \boldsymbol{e}_z)^2$ with $W = \int dz M_1 S(\partial_z \phi)^2$.

Next we consider dynamics. Because of the complexity of the system, we are restricted to a phenomenological description by a minimal set of equations. The displacement field follows a convective equation

$$\frac{\partial \boldsymbol{u}}{\partial t} = \boldsymbol{v} \cdot (\mathrm{I} - \nabla \boldsymbol{u}), \tag{8}$$

where the velocity $\boldsymbol{v}$ of the network is given by[11,12]

$$\boldsymbol{v} = Z^{-1}\boldsymbol{g}. \tag{9}$$

The latter equation describes a balance between dissipative and non-dissipative (elastic) forces, and $Z$ is the frictional coefficient. In writing Eq.(9), we have assumed that hydrodynamic effects due to solvent flow is negligible. The same assumption leads us to a model-A type equation for the orientational order parameter,

$$\frac{\partial Q_{ij}}{\partial t} = -\Gamma \frac{\delta F}{\delta Q_{ij}}, \tag{10}$$

where $\Gamma$ is the inverse of the rotational viscosity coefficient.

## NUMERICAL SIMULATION

The phase separation process was studied by numerical simulation using the above-defined TDGL model. Our choice of the static parameters is $N = 100, N_s = 10, \chi = 0.13, L = 0.5, M_0 = 100$, and $M_1 = 30$. The Maier-Saupe interaction parameter is set at $w = 2.5$, which locates the I-N transition at $\phi = 0.2$. The kinetic coefficients

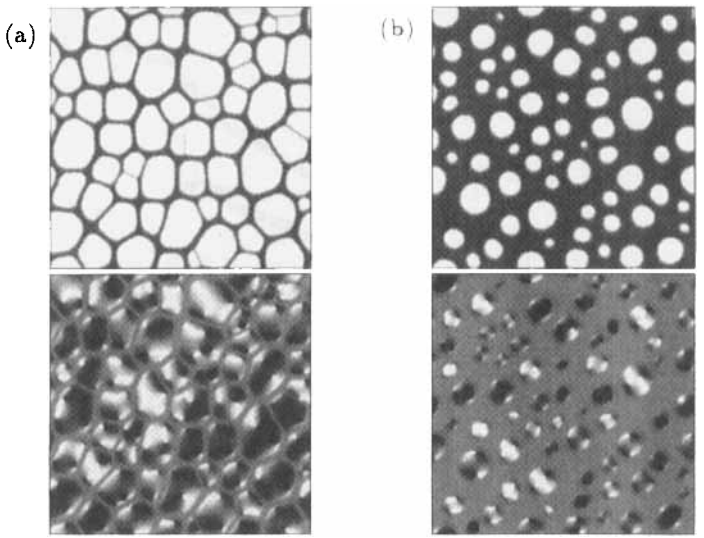


FIGURE 1: Snapshots of polymer concentration $\phi$ (above) and orientational order parameter $Q_{xy}$ (below). (a) $\phi_0 = 0.5$ at time $t = 1000$. (b) $\phi_0 = 0.3$ at $t = 1000$.

are chosen as $Z^{-1} = \Gamma = 1.0$. The kinetic equations (8) and (10) are integrated on a $256 \times 256$ periodic lattice with the grid size $\Delta x = 1$, using the Euler scheme with a variable time step.

In Fig.1, we show real-space snapshots of the composition and order parameter fields. For a small average polymer fraction $\phi_0 = 0.3$, a foam-like morphology with polyhedral droplets is obtained. On the other hand, we find spherical droplets for a larger average polymer fraction $\phi_0 = 0.5$. These are in good qualitative agreements with experimental observations. In particular, a foam-like morphology as in Fig.1(a) has been clearly observed by confocal microscopy[4,5]. As to the director texture, each of the spherical droplets quite regularly contains a single pair of defects, while many of the non-spherical droplets contain more than two couples of defects. Interaction between domain shape and director texture is a subject left to future systematic study. Non-spherical domain shapes presumably create metastable minima of the Frank free energy, which trap multi-pair defects.

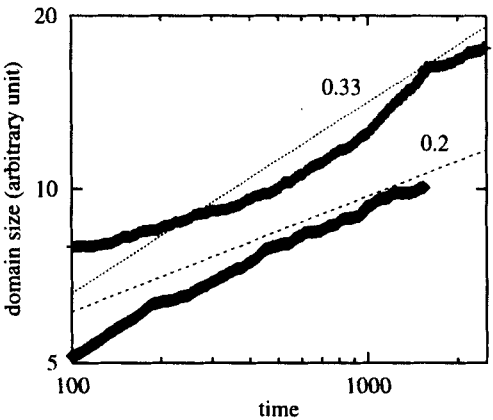


FIGURE 2: Temporal evolution of the characteristic domain size for $\phi_0 = 0.5$ (above) and $\phi_0 = 0.3$ (below). For ease of view, different units of length are used for the two cases. Compare with the power law with exponents $\beta = 0.33$ and 0.2.

The origin of the foam-like morphology in Fig.1(a) can be inferred from previous studies of phase separation in isotropic gels[11,12]. In analogy to real foams, the morphology is supported by mechanical tension in the rim of each domain. At the phase boundary, network meshes are required to be continuous while there is a volume mismatch between the two phases. As a result, the polymer-rich matrix is stretched in parallel to the phase boundary[13].

Temporal evolution of the characteristic domain size $R = R(t)$ is shown in Fig.2. For $\phi_0 = 0.3$, the effective growth exponent $\beta = \ln R / \ln t$ in the late stage was $0.20 - 0.22$, substantially smaller than the scaling value $1/3$ expected in the absence of elasticity. For $\phi_0 = 0.5$, the exponent transiently exceeded $1/3$, and a slowing occurred at the latest stage of simulation. We did not reach a complete freezing of the pattern in our simulation time.

## NEMATIC GELS

In PDLCs, the anisotropic nature of the solvent is not important

in determining the domain morphology. Interaction between liquid-crystallinity and rubber-elasticity is more evident in nematic gels, in which nematogens are woven into the network itself. Characteristic of this system is an energetic coupling between strain and orientation[14]. Such anisotropic gels in a (micro-)phase-separated state have been studied also for application in electro-optical devices[15]. For simplicity, here we consider a network originally crosslinked in the isotropic phase. If the gel is then brought into the nematic phase, the director tends to be parallel to the direction of external stretching, reflecting the anisotropic conformation of liquid-crystalline polymers[14]. This strain-orientation coupling gives rise to a novel interfacial effect in phase separation; the anisotropic strain created by the volume mismatch acts on the director and makes it parallel to the phase boundary. This effective anchoring strongly suppresses director reorientation under an electric field. A detailed account of the result, supported by a numerical simulation, will be presented elsewhere.

## CONCLUSION

In PDLCs, we find a slow coarsening kinetics as well as an asymmetric foam-like morphology, both of which are explained as rubber-elastic effects. The interfacial volume mismatch, which is responsible for the asymmetric morphology, causes an indirect anchoring in nematic polymer gels.

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## APPENDIX

The Maier-Saupe free energy of a two-dimensional solution of rod-like molecules is given by

$$H_{MS} = \frac{\phi_{LC}}{N_s}\left[-\ln \mathcal{Z} + \frac{\phi_{LC} w S^2}{2}\right], \tag{11}$$

$$\mathcal{Z} = \int_{-1}^{1} d(\cos\theta) \exp\left[\phi_{LC} w S P_2(\cos\theta)\right], \tag{12}$$

where $w$ is the interaction parameter, $\theta$ is the angle between the director and the rod, $S = \langle P_2(\cos\theta)\rangle$ is the scalar order parameter, and $\phi_{LC} = 1 - \phi$. The I-N transition occurs at $\phi_{LC} = 2/w$. Minimizing $H_{MS}$ with respect to $S$, we obtain the equilibrium free energy $\tilde{H}_{MS}(\phi)$ and the equilibrium order parameter $\tilde{S}(\phi)$. By identifying these with the corresponding quantities in the Landau-de Gennes model, which are $-A^2(\phi)/4C(\phi)$ and $\sqrt{-A(\phi)/2C(\phi)}$ respectively, we obtain the functions $A(\phi)$ and $C(\phi)$.

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