

Classification
Physics Abstracts
64.70 — 64 60 — 61 30

Spinodal decomposition in liquid crystalline materials

A. Ten Bosch

Laboratoire de Physique de la Matière Condensée (*), Parc Valrose, 06034 Nice Cedex, France

(Received 5 December 1990, accepted in final form 26 April 1991)

Abstract. — The theory of phase separation in a liquid crystal by spinodal decomposition is developed. The time evolution of two coupled parameters, the volume concentration (or mole fraction), and the orientational order parameter is calculated. The conditions for periodic fluctuations are given and the structure factor for spinodal decomposition is studied.

1. Introduction.

The dynamics of phase separation in incompatible solid or fluid mixtures has been studied experimentally as well as theoretically in a large number of different systems from polymers to metals [1]. Cahn [2] proposed long ago that, besides the usual phase separation in the metastable region by nucleation and droplet growth, a different process, called spinodal decomposition, may occur in the unstable region of the phase diagram. The predicted structure is described in terms of a superposition of periodic modulations of a fixed wave length, random in amplitude, orientation and phase. On the other hand, Binder [1, 3] from results on numerical simulation of cluster growth, suggested that there is no evidence of a sharp distinction between metastable and unstable states and that the process of spinodal decomposition can be viewed as a generalized nucleation phenomenon.

Interest in this problem has been revived by the advent of a new type of material: liquid crystal polymers, and by the industrial applications of this material in composite design. Periodic *versus* random dispersed structures could be advantageous for mechanical (or other) properties of the composite and it is desirable to control and understand the fundamental processes of phase separation in these systems. New experiments in the biphasic region of liquid crystal polymer mixtures have been reported. Anisotropic droplets [4] and even needle type structures [5] have been observed and unusual periodic structures [6] are formed during unmixing. Recently neutron scattering experiments have shown evidence of spinodal decomposition in the structure factor [7]. In the present paper we investigate spinodal decomposition in a liquid crystal mixture. In a simple model we show that concentration fluctuations need not be accompanied by order parameter fluctuations and that the range of instability, the critical wave length and the growth rate for spinodal decomposition are not affected by the presence of liquid crystal order for a quench from the isotropic phase.

(*) C N R S.U.A 190

2. Theory for early time behavior.

2.1 SIMPLE SOLVENTS — We consider first a solution of a mesomorphic component in a non-mesomorphic material (simple solvent or polymer). As discussed in the Appendix, the free energy is given by

$$F = \int \left[f(\psi, \sigma) + \frac{K_\psi}{2} (\nabla\psi)^2 + \frac{K_\sigma}{2} (\nabla\sigma)^2 \right] dv. \quad (2.1)$$

Here $f(\psi, \sigma)$ is the mean field free energy density of the initially homogenous material of composition ψ of mesomorphic component with nematic order parameter S . It has been useful to define the « order parameter » σ as the product of ψ and the usual nematic order parameter S . The model free energy can then be written as a function of ψ and σ alone.

$$f(\psi, \sigma) = g(\psi) - \psi L(\sigma) - \frac{u\sigma^2}{2} \quad (2.2)$$

with the isotropic part

$$\frac{g(\psi)}{KT} = \frac{\psi}{L} \ln \psi + (1 - \psi) \ln (1 - \psi) + \psi(1 - \psi) \chi$$

$L(\sigma)$ is the orientational entropy, which does not need to be considered in more detail, and u is the nematic mean field. The degree of polymerization is given by L , χ is the isotropic interaction parameter.

On expanding the free energy to include spatial variations in composition and order parameter [9], again only terms in $\nabla\psi$ and $\nabla\sigma$ occur

We therefore write in (2.1) terms in K_ψ and K_σ due to composition and « order parameter » fluctuations respectively. The kinetics of this systems are given by solutions of the dynamic equations [1] for the conserved order parameter

$$\frac{\partial\psi}{\partial t} = \Gamma \nabla^2 \left(-K_\psi \nabla^2 \psi + \frac{\partial f(\psi, \sigma)}{\partial \psi} \right) \quad (2.3)$$

and for the nonconserved order parameter σ

$$\frac{\partial\sigma}{\partial t} = \gamma \left(K_\sigma \nabla^2 \sigma - \frac{\partial f(\psi, \sigma)}{\partial \sigma} \right) \quad (2.4)$$

Γ and γ are mobilities for concentration of order parameter diffusion processes respectively.

As usual [2], we look for a solution

$$\begin{aligned} \psi &= \psi_0 + \delta\psi \\ \sigma &= \sigma_0 + \delta\sigma \end{aligned} \quad (2.5)$$

where (ψ_0, σ_0) defines the initial average concentration and order parameters which fulfill the stationary state conditions

$$\begin{aligned} \psi_0 \frac{\partial L}{\partial \sigma_0} + u\sigma_0 &= \frac{\partial f}{\partial \sigma_0} = 0 \\ \frac{\partial g}{\partial \psi_0} - L(\sigma_0) &= \frac{\partial f}{\partial \psi_0} = \mu. \end{aligned} \quad (2.6)$$

Here μ is a generalized chemical potential [8]. We consider a spatially homogenous initial state and $(\delta\psi, \delta\sigma)$ denote the fluctuations around these values

The linearised equations in Fourier space are

$$\omega \begin{pmatrix} \delta\psi \\ \delta\sigma \end{pmatrix} = M \begin{pmatrix} \delta\psi \\ \delta\sigma \end{pmatrix}. \quad (2.7)$$

Where the matrix is given by

$$M = \begin{pmatrix} -\Gamma q^2(q^2 K_\psi + \alpha) & \Gamma q^2 \frac{\partial L}{\partial \sigma_0} \\ \gamma \frac{\partial L}{\gamma \sigma_0} & -\gamma(q^2 K_\sigma + \beta) \end{pmatrix}. \quad (2.8)$$

In order to obtain a nontrivial solution, the determinant of the coefficients must vanish. This condition results in a relation between ω and q

$$(\omega + \Gamma q^2(q^2 K_\psi + \alpha)) (\omega + \gamma(q^2 K_\sigma + \beta)) - \gamma \Gamma q^2 \left(\frac{\partial L}{\partial \sigma_0} \right)^2 = 0. \quad (2.9)$$

The two control parameters are $\alpha = \frac{\partial^2 f}{\partial \psi_0^2}$, $\beta = \frac{\partial^2 f}{\partial \sigma_0^2}$

We will concentrate here on the case of a quench from the initial disordered state $(r_0 = 0 \text{ and } \frac{\partial L}{\partial \sigma_0} = 0)$

We find a solution $\omega > 0$ for a finite range of wave vectors from the first parenthesis of equation (2.9) identical to the Cahn-Hilliard theory [1, 2]. The condition on the concentration ψ_0 of the initial state is $\alpha < 0$ or $\frac{\partial^2 f}{\partial \psi_0^2} < 0$ as in non mesomorphic systems.

Schematically, the mixing free energy as a function of mole fraction ψ at constant temperature can be given as an isotropic branch ($\sigma = 0$) at low values of ψ and an anisotropic branch ($\sigma = 0$) at high values of ψ . Phase separation occurs between points of equal chemical potential. The two phases can be both isotropic or one isotropic and one anisotropic phase [10]. The limits for stability or metastability of the quenched fluid phase are given by the conditions for the spinodal of the isotropic branch. Within the spinodal region of the isotropic branch, phase separation could take place though periodic composition modulations

For a quench from an initial isotropic state $\sigma_0 \neq 0$, the equations (2.7) are decoupled. The order parameter σ is stable and we have a positive eigenvalue associated with the instability in concentration ψ . Similar to the results on He³-He⁴ [1, 20], the initial behaviour of the system after quench is one in which the conserved order parameter ψ evolves towards a local equilibrium state while the nonconserved order parameter remains essentially constant (and equal to zero). The local equilibrium state for ψ will correspond to one of the two equilibrium states ψ_+ or ψ_- on the isotropic branch. The transition to a stable anisotropic state could then take place, for example, through nucleation of the anisotropic minority phase.

In principal, a quench from an initial homogenous anisotropic phase with $\sigma_0 > 0$ into a biphasic zone is also feasible but has not yet been studied experimentally. The situation is then more complex and has not been analyzed here. A new type of spinodal decomposition with coupled composition and order parameter fluctuations may then be possible from equation (2.9).

2.2 BINARY MESOMORPHIC MIXTURES. — We now go on to the experimental situation of interest of a binary mixture of mesomorphic components. The model free energy in this case is given as

$$F = \int dr \left[f(\psi, \sigma_1, \sigma_2) + \frac{K_\psi}{2} (\nabla\psi)^2 + \frac{K_{11}}{2} (\nabla\sigma_1)^2 + K_{12}(\nabla\sigma_1 \cdot \nabla\sigma_2) + \frac{K_{22}}{2} (\nabla\sigma_2)^2 \right]. \quad (2.10)$$

Again $f(\psi, \sigma_1, \sigma_2)$ is the free energy density of the initial homogeneous phase. The composition of component 1 is given by ψ , that of component 2 by $(1 - \psi)$. The respective orientational « order parameters » are then σ_1 and σ_2 , again products of the usual nematic order parameters of the components S_1 and S_2 and the relevant concentrations: $\sigma_1 = \psi S_1$, $\sigma_2 = (1 - \psi) S_2$ (see Appendix). The terms in K_ψ , K_{11} , K_{22} and K_{12} take compositional (K_ψ) and order parameter (K_{ij}) fluctuations into account. The model free energy can be written as before [8, 10].

$$f(\psi, \sigma_1, \sigma_2) = g(\psi) - L(\psi, \sigma_1, \sigma_2) \quad (2.11)$$

where

$$\frac{g(\psi)}{KT} = \frac{\psi}{L_1} \ln \psi + \frac{(1 - \psi)}{L_2} \ln (1 - \psi) + \psi(1 - \psi) \chi$$

$$L(\psi, \sigma_1, \sigma_2) = \psi L_1(\sigma_1, \sigma_2) + (1 - \psi) L_2(\sigma_1, \sigma_2) - \frac{1}{2} (u_{11} \sigma_1^2 + u_{22} \sigma_2^2 - 2 u_{12} \sigma_1 \sigma_2)$$

$L_1(\sigma_1, \sigma_2)$ and $L_2(\sigma_1, \sigma_2)$ are the orientational entropies of the two liquid crystalline components and the terms in u_{ij} are the contributions from the nematic mean fields. L_1 and L_2 are the degrees of polymerization. Three dynamic equations now control the kinetics of phase separation; one for the conserved variable ψ

$$\frac{\delta\psi}{\delta t} = \Gamma \nabla^2 \left(-K_\psi \nabla^2 \psi + \frac{\partial f}{\partial \psi}(\psi, \sigma_1, \sigma_2) \right) \quad (2.12)$$

and two for the non-conserved variables σ_1, σ_2

$$\begin{aligned} \frac{\partial\sigma_1}{\partial t} &= \gamma_1 \left(K_{11} \nabla^2 \sigma_1 + K_{12} \nabla^2 \sigma_2 - \frac{\partial f}{\partial \sigma_1}(\psi, \sigma_1, \sigma_2) \right) \\ \frac{\partial\sigma_2}{\partial t} &= \gamma_2 \left(K_{22} \nabla^2 \sigma_2 + K_{12} \nabla^2 \sigma_1 - \frac{\partial f}{\partial \sigma_2}(\psi, \sigma_1, \sigma_2) \right). \end{aligned} \quad (2.13)$$

As before we investigate the existence of periodic fluctuations $(\delta\psi, \delta\sigma_1, \delta\sigma_2)$ around an initial isotropic phase.

After linearization of equations (10) and (11), the condition for existence of nontrivial solutions leads to the dispersion relation. For an initial isotropic state with $\sigma_1 = \sigma_2 = 0$, we find for the linearized equations in Fourier space:

$$\omega \begin{pmatrix} \delta\psi \\ \delta\sigma_1 \\ \delta\sigma_2 \end{pmatrix} = M \begin{pmatrix} \delta\psi \\ \delta\sigma_1 \\ \delta\sigma_2 \end{pmatrix}. \quad (2.14)$$

Where the linearized matrix is now

$$M = \begin{pmatrix} -\Gamma q^2(K_\psi q^2 + \alpha) & 0 & 0 \\ 0 & & -\Sigma \\ 0 & & \end{pmatrix} \tag{2.15}$$

$$\Sigma = \begin{pmatrix} \gamma_1(K_{11} q^2 + \beta_{11}) & \gamma_1(K_{12} q^2 + \beta_{12}) \\ \gamma_2(K_{12} q^2 + \beta_{12}) & \gamma_2(K_{22} q^2 + \beta_{22}) \end{pmatrix}.$$

The control parameters are

$$\alpha = \frac{\partial^2 F}{\partial \psi^2}, \quad \beta_{ij} = \frac{\partial^2 F}{\partial \sigma_i \partial \sigma_j}$$

The condition for a non-trivial solution is then $\det M = 0$ or

$$(\omega - \Gamma q^2(\alpha + K_\psi q^2)) \det \Sigma = 0.$$

Again the composition and order parameter instabilities are decoupled. We find an instability for ψ equivalent to the spinodal of isotropic mixtures for which σ_1 and σ_2 remain constant (and equal to zero). A second instability for σ_1 and σ_2 at constant ψ also exists for certain values of material constants and has been discussed previously [11]. Which of the two instabilities will be chosen depends on the initial concentration, the final temperature and the parameters of the mixture, in particular the phase diagram. The instability in composition occurs for quenches within the spinodal curves of the isotropic mixture. The instability in order parameter occurs for $T < T^*$, the limiting temperature for metastability of a stable isotropic state in the mixture. At a given temperature, this requires that the initial concentration correspond to a value for which the isotropic phase is unstable after the quench. The order parameter then evolves towards the value corresponding to lower energy anisotropic phase (Figs 1, 2)

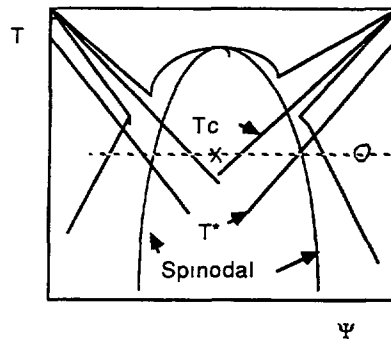


Fig 1 — Typical phase diagram for a mixture of two mesogenic components. The critical temperatures T_c (limate of stability of isotropic phase) and T^* (limit of instability of isotropic phase) are given. A typical quench from the isotropic phase to within the spinodal (x) or to within the anisotropic zone (o) is marked.

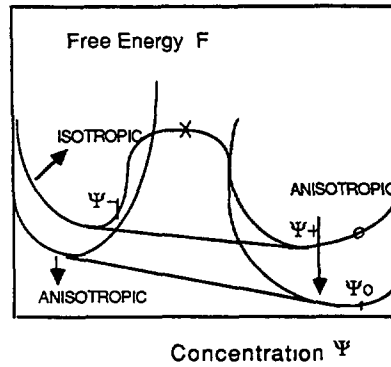


Fig 2 — Typical free energy plot corresponding to figure 1. If the quench results in point X spinodal decomposition of composition could occur leading to a separation in isotropic states ψ_+ , ψ_- . If the quench results in point O, periodic fluctuations of order parameter could occur leading to an anisotropic state ψ_0 .

3. Calculations of the structure factor [12, 13].

3.1 SOLUTIONS IN A NON-MESOMORPHIC SOLVENT — We study first solutions in a non-mesomorphic solvent. In these systems three correlation functions can be defined $\langle \delta\psi_q \delta\psi_{-q} \rangle$, the fluctuation of concentration, given by the Fourier transform $\delta\psi_q$, $\langle \delta\sigma_q \delta\sigma_q \rangle$, the fluctuation of « order parameter » given by $\delta\sigma_q$, and the cross coupling correlation function $\langle \delta\sigma_q \delta\psi_q \rangle$.

These functions can be calculated from the set of dynamic equations (2.6). Following the method of references [12] and [13], we must supplement these equations by a random force

$$G(t) = \begin{pmatrix} \eta_q \\ \xi_q \end{pmatrix}$$

$$\frac{\partial}{\partial t} \begin{pmatrix} \delta\psi_q \\ \delta\sigma_q \end{pmatrix} = M \begin{pmatrix} \delta\psi_q \\ \delta\sigma_q \end{pmatrix} + \begin{pmatrix} \eta_q \\ \xi_q \end{pmatrix} \tag{3.1}$$

Where M is the linear matrix given earlier in (2.8). In vector form we write

$$\frac{\partial}{\partial t} \alpha(t) = M\alpha(t) + G(t) \tag{3.2}$$

with

$$\alpha(t) = \begin{pmatrix} \delta\psi_q \\ \delta\sigma_q \end{pmatrix}$$

We will investigate here only correlations over sufficiently large distances, so that the structure of the particles will not play a role. The linear equation (3.2) is solved as usual

$$\alpha = \alpha_0 e^{Mt} + e^{Mt} \int_0^t e^{-Mt'} G(t') dt' \tag{3.3}$$

leading to the correlation functions given by the dyad

$$\begin{aligned} (\alpha \alpha^*)_{ik} &= \alpha_i \alpha_k^* \\ \langle \alpha \alpha^* \rangle &= e^{2Mt} [\langle \alpha_0 \alpha_0^* \rangle + (2M)^{-1} Q(q)] - (2M)^{-1} Q(q). \end{aligned} \tag{3.4}$$

We have used the following relations which hold by definition [14]:

$$\begin{aligned} \langle G(t) \rangle &= 0 \\ \langle G(t) G(t') \rangle &= Q(q) \delta(t - t') \end{aligned} \tag{3.5}$$

and the coefficient $Q(q)$ is related to the Onsager coefficients

$$Q(q) = 2KT \begin{pmatrix} \Gamma_q^2 & 0 \\ 0 & \gamma \end{pmatrix}. \tag{3.6}$$

It is now simple to derive the static correlation functions

$$\langle \alpha \alpha^* \rangle_s = - (2M)^{-1} Q(q). \tag{3.7}$$

For a quench from the isotropic state, we find for the static structure factor

$$\langle |\delta \psi_q|^2 \rangle = \frac{KT}{K_\psi q^2 + \frac{\partial^2 g}{\partial \psi_0^2}} \tag{3.8}$$

The concentration fluctuations give identical behaviour to spinodal decomposition in isotropic liquid mixtures. As in these systems, the static structure factor shows a divergency at a critical wave length $q_s^2 = - \frac{\partial^2 g}{\partial \psi_0^2} \cdot \frac{1}{K_\psi}$. If the concentration ψ_0 is within the isotropic spinodal, exponential growth of the intensity with time is predicted [14]. The cross coupling correlation functions are zero and for the order parameter fluctuations we find

$$\langle |\delta \sigma_q|^2 \rangle = \frac{2KT}{K_\sigma q^2 - \psi_0 \frac{\partial^2 L}{\partial \sigma_0^2} - u} \tag{3.9}$$

This is same form as for homophase fluctuations of the order parameter in the isotropic phase [15]. The typical divergency at $q = 0$ of the amplitude at the temperature T^* of the mixture is found T^* is thus the temperature below which the isotropic phase is absolutely unstable, and given here by

$$\frac{\partial f}{\partial \sigma} = \frac{\partial^2 f}{\partial \sigma^2} = 0, \quad \sigma = 0.$$

3.2 BINARY MIXTURE OF MESOGENS. — An identical treatment can be made in the case of a mixture of two liquid crystal components. For example, two liquid crystal polymers of different degree of polymerization, or a solution of a liquid crystal and a polymer liquid crystal have been studied in optical and in neutron scattering experiments. In this case two order parameters on each of the components exist. The correlation functions of interest are the fluctuation of concentration, and the fluctuation of total «order parameter» $\sigma = \sigma_1 + \sigma_2$. The linear matrix for a quench from the isotropic state is given by (2.15) and the static structure factor is again of the form (3.8) with behaviour as discussed in 3.1. On the other hand the order parameter fluctuations are given by

$$\langle |\delta \sigma_q|^2 \rangle = \frac{KT \gamma_1 \gamma_2}{\det \Sigma} (-q^2(K_{11} + K_{22} - 2K_{12}) + 2\beta_{12} - \beta_{11} - \beta_{22}). \tag{3.10}$$

As discussed in 2.2 and in reference [11], a second type of «spinodal» can exist, with a critical

wave vector for divergency of the scattered amplitude, which follows from the condition $\det \Sigma = 0$

Decay of the isotropic state through periodic variations of the order parameter can occur for a quench from the isotropic phase if the initial concentration corresponds to a value greater than the limit of metastability of the isotropic phase. The concentration remains constant during this process (Fig 1, 2).

Discussion.

In conclusion, we have investigated the existence of periodic instabilities in the concentration and in the nematic order parameter for liquid crystal mixtures. We have concentrated on the early stage, coarse grained limit of the phase separation. We have shown that for a solution of a liquid crystal in a simple solvent, the usual isotropic spinodal composition occurs for incompatible components when quenched from the homogenous isotropic phase. This results in a local metastable isotropic phase and can then be followed by a phase transition by nucleation to a stable anisotropic phase if such a phase exists at the final concentration after phase separation. For a mixture of two liquid crystal components, the same scenario can take place. In addition in certain materials, if the quench leads to an unstable (relative to the anisotropic phase) isotropic phase, a periodic instability of the order parameter can occur for which the concentration remains constant and which leads to a stable anisotropic phase.

In this paper, we have assumed the director fluctuations to be damped and the director to be fixed parallel to an external magnetic field. Director fluctuations have been studied in reference [16] and may be important in non-oriented samples. Strong correlations in position may lead to concentration dependence of the constants of the gradient terms K_σ , K_ψ etc. This would lead to higher order terms and a different concentration dependence of the correlation lengths of the fluctuations. Such effects have been studied in isotropic polymer mixtures [12]

We have concentrated on the quench from the isotropic phase which corresponds to the present experimental procedure and the present work applies to side chain [17] as well as main chain [7] liquid crystal polymers. Concentration fluctuations with spinodal type behavior should be visible in small angle neutron scattering for which order parameter fluctuations would be negligible. The case of light scattering is more complex, both concentration [18, 19] and order parameter [15] fluctuations playing a role. Late stage dynamics [20] can also be observed and would be of interest to study as well as critical behavior [21] as has been done in the related case of phase separation with coupled conserved and nonconserved order parameters in $\text{He}^3\text{-He}^4$ mixtures [22].

Appendix.

The free energy density of a solution of a liquid crystal polymer and a simple solvent has been derived in a mean field approximation [8]

$$f(\psi, \sigma) = \left[\frac{\psi}{L} \ln \psi + (1 - \psi) \ln (1 - \psi) + \psi (1 - \psi) \chi \right] KT - \psi L(S, \psi) - \psi^2 u S^2 / 2 \quad (\text{A1})$$

ψ is the volume concentration of the liquid crystal polymer with nematic polymer S . The first terms give the isotropic part; the entropy of mixing and the isotropic interactions. The fourth term $L(S, \psi)$ is calculated from the chain partition function and depends on the model of the liquid crystal chain. The final term is the mean field contribution from the nematic interaction u corrected for the effect of dilution by a factor ψ . The expression derived in (8) for u is a spatial average of the pairwise orientation dependent interaction.

The free energy of deformation $f_d(r)$ in orientation dependent systems is given in reference [9].

$$(x_\alpha = (x, y, z))$$

$$F_d(r) = \sum_{\alpha\beta} \int c_{\alpha\beta}(\mathbf{w}, \mathbf{w}') \frac{\partial}{\partial x_\alpha} \rho(\mathbf{r}, \mathbf{w}) \frac{\partial}{\partial x_\beta} \rho(\mathbf{r}, \mathbf{w}) d\mathbf{w} d\mathbf{w}'. \quad (\text{A2})$$

The distribution function of position \mathbf{r} and orientation \mathbf{w} is $\rho(\mathbf{r}, \mathbf{w})$ and the term $c_{\alpha\beta}(\mathbf{w}, \mathbf{w}')$ is related to the direct correlation function in the homogenous material. We consider monodomain samples of uniform alignment \mathbf{n} .

For systems characterized by a second order expansion in Legendre Polynomials $P_\ell(w)$ for a Maier-Saupe type of anisotropic potential

$$c_{\alpha\beta}(\mathbf{w}, \mathbf{w}') = \sum_{\ell=0,2} c_{\alpha\beta,\ell} P_\ell(\mathbf{w}) P_\ell(\mathbf{w}') \quad (\text{A3})$$

We set as usual $\rho(\mathbf{r}, \mathbf{w}) = \psi(r) f(\mathbf{r}, \mathbf{w})$, where $f(r, w)$ is the orientational distribution function [23]. Then $\int f(r, w) dw = 1$ With the usual definition of the local nematic order parameter $\int f(r, w) P_2(w) dw = S(r)$, we find

$$\int \rho(\mathbf{r}, \mathbf{w}) P_2(\mathbf{w}) d\mathbf{w} = \psi(r) S(r) = \sigma(r). \quad (\text{A4})$$

From (A2) to (A4), we obtain

$$F_d(r) = \sum_{\alpha\beta} \left(c_{\alpha\beta,0} \frac{\partial}{\partial x_\alpha} \psi(r) \frac{\partial}{\partial x_\beta} \psi(r) + c_{\alpha\beta,2} \frac{\partial}{\partial x_\alpha} \sigma(r) \frac{\partial}{\partial x_\beta} \sigma(r) \right). \quad (\text{A5})$$

Consistent with the symmetry of the nematic for a radial distribution of liquid crystal entities, equation (A5) simplifies to

$$F_d(r) = \frac{K_\psi}{2} (\nabla\psi(r))^2 + \frac{K_\sigma}{2} (\nabla\sigma(r))^2. \quad (\text{A6})$$

If the angular dependence of distance dependent correlations are considered in (A3), a term in $(\mathbf{n} \cdot \nabla\sigma)^2$ will appear in (A6) and lead to direction dependent order parameter fluctuations [15]. In nonaligned samples fluctuations in the director \mathbf{n} could also occur [15].

The K_ψ term is well known from interfacial and dynamic studies on incompatible mixtures [12]. The term in the elastic constant K_σ relative to the nematic order parameter $(\nabla S)^2$ has been used in studies of the biphasic of pure liquid crystals [15, 23]. In the present case, coupling between order parameter and concentration gradients also occurs.

To derive the model free energy in the mixture of mesomorphic components, the procedure is identical. The nematic order parameters on each individual component are given by S_1 and S_2 , the volume concentrations are ψ and $1 - \psi$. As before, we find that the free energy density can be written as a function of ψ , $\sigma_1 = \psi S_1$ and $\sigma_2 = (1 - \psi) S_2$ and their gradients.

References

- [1] GUNTON J D., SAN MIGUEL M., chapt 3, « Phase transitions and critical phenomena », Eds C. Domb, J C Lebowitz, Vol 8 (Academic Press, London, 1983)
- [2] CAHN J. W., *J Chem Phys* **42** (1965) 93.
- [3] BINDER K., STAUFFER D., *Adv Phys* **25** (1976) 343.
- [4] CASAGRANDE C., VEYSSIE M., KNOBLER C M., *Phys Rev. Lett* **58** (1987) 2079.
- [5] D'ALLEST J F., Thesis, University of Nice (1988)
- [6] CASAGRANDE C., FABRE P., GUEDEAU M A., VEYSSIE M., *Europhys Lett* **3** (1987) 73
- [7] FRIED F., LANSAC Y., SIXOU P., BLUMSTEIN A., BLUMSTEIN R., 33 IUPAC Symposium on Macromolecules, Montreal (1990)
- [8] TEN BOSCH A., PINTON J., MAÏSSA P., SIXOU P., *J. Phys A* **20** (1987) 453
- [9] PONIEWIERSKI A., STECKI J., *Mol. Phys* **38** (1979) 1931
- [10] MAÏSSA P., SIXOU P., *Liquid Crystals* **5** (1989) 1861
- [11] LANSAC Y., TEN BOSCH A., *J Chem Phys* (in press)
- [12] BINDER K., *J Chem Phys* **79** (1983) 6387
- [13] COOK H E., *Acta Metallurgica* **18** (1970) 297
- [14] METIU H., KITAHARA K., ROSS J., Chapt. 4 in « Fluctuation Phenomena », Eds. E W Montroll, J L. Lebowitz (North Holland Physics Publishing, Amsterdam, 1976).
- [15] SHENG P., PRIESTLEY E B., Chapt 10 in « Introduction to liquid crystals », Eds ED B Priestley, P Wojtowicz, P Sheng (Plenum Press, New York, 1974).
- [16] SHIMADA T., DOI M., OKANO K., *J Chem Phys* **88** (1988) 2815 ,
DOI M., SHIMADA T., OKANO K., *J Chem Phys.* **88** (1988) 4070
- [17] NOIREZ L., thesis, Univ Orsay (1989) p 167
- [18] VAN DER SCHOOT P., ODIJK T., *J Chem Phys* **93** (1990) 3580
- [19] KOBERSTEIN J., RUSSELL T. P., STEIN R. S., *J. Polymer Sci (Polym Phys. Ed)* **17** (1979) 1719.
- [20] SAN MIGUEL M., GUNTON J D., DEE G., SAHNI P S., *Phys Rev B* **23** (1981) 2334
- [21] HOHENBERG P C., HALPERIN B I., *Rev Mod Phys* **49** (1977) 435.
- [22] HOHENBERG P C., NELSON D R., *Phys Rev. B* **20** (1979) 2665
- [23] TELO DA GAMA M M., THURTELL J H., *J Chem Soc Faraday Trans.* **82** (1986) 1721