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Dynamics of phase separation in mesomorphic mixtures

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We describe the dynamics of phase separation and transition processes, in binary mesomorphic mixtures with the help of a system of two coupled partial derivative equations. We emphasize, both analytically and numerically, that, depending on the regions of the phase diagram, the dynamical behaviour may result either from a two step process (first the phase transition, then the phase separation) or from a process showing salient features of the Cahn–Hilliard spinodal decomposition (bicontinuous periodic networks in the transient stages). The dynamics of evolution of the domain patterns are illustrated with the help of numerical simulations in which homeotropic and planar anchorages are visualized.

1. Introduction

Studies on mesomorphic materials (small molecules or polymer liquid crystals) have attracted great interest (experimental and theoretical) during these last years. It often happens that these materials, to be efficiently used, must be diluted in a solvent or mixed with a conventional (non-mesomorphic) polymer. While the dynamics of phase separation of isotropic fluid (small molecules or polymers) mixtures have been extensively studied both experimentally and theoretically [1–4], the behaviour of mesomorphic blends is relatively less well known, although some observations on phase separation in nematic solutions have been recently made [5–9] and theoretical models proposed [10, 11, 12].

Then, we have systems in which there is a coupling between phase separation and phase transition processes. The former is theoretically described by a scalar conservative order parameter ϕ (concentration of one of the two species) solution of a Cahn–Hilliard non-linear partial derivative equation, while the second one is depicted by a scalar non-conservative orientational order parameter S solution of a Ginzburg–Landau non-linear partial derivative equation. S illustrates the degree of orientation of the molecules with respect to the most favourable direction of the medium—the director, which is rendered uniform in the whole sample by application, for example, of a uniform magnetic field.

With the help of a free energy formulation and taking into account the effects of concentration and orientation, together with their spatial variations, we derive the two coupled dynamical equations describing this system and we give its qualitative behaviour at shorter and longer times by using numerical simulations.

2. Theory

2.1. Dynamical equations

We are interested in mixtures with no more than one mesomorphic component, which may be a small molecule liquid crystal or a polymeric liquid crystal. As for pure mesomorphic compounds or non-mesomorphic binary mixtures (for example, conventional polymers, simple liquids ...), this system can reach a metastable or unstable zone depending on the temperature and the concentration at which the experiment is prepared. The system is out of equilibrium and evolves towards a most favourable thermodynamical state. We suppose that this evolution is governed by the variations in the free energy, which, in the case of two order parameters and keeping in mind the spatial inhomogeneities, is [13]

$$\mathcal{F} = \int \left(f(\phi, S) + \frac{K_1}{2} (\nabla \phi)^2 + \frac{K_2}{2} (\nabla(\phi S))^2 + \frac{K_3}{2} (\hat{n} \cdot \nabla(\phi S))^2 \right) d\mathbf{r} \quad (1)$$

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where K_1, K_2, K_3 are phenomenological coefficients (K_1 is

related to a translational diffusion coefficient and is always positive, while K_2 and K_3 are related to orientational diffusion coefficients such that $K_2 > 0$ if $\hat{n} \perp \nabla S$ or $K_2 + K_3 > 0$ if $\hat{n} \parallel \nabla S$ [14]) and $f(\phi, S)$ is the homogeneous free energy density which permits us to define the various phases present as a function of concentration and temperature [15] (phase diagram, figure 2), ϕ is the volume concentration of the mesomorphic component and S is the orientational order parameter (estimated with respect to the director which is uniform in the sample). We have

$$f(\phi, S) = \frac{\phi}{L_A} \log(\phi) + \frac{1-\phi}{L_B} \log(1-\phi) + \chi\phi(1-\phi) + \frac{\phi}{L_A} ((A\phi^2 + D\phi)S^2 - B(\phi S)^3 + C(\phi S)^4) \quad (2)$$

where $L_i (i = A, B)$ are the degrees of polymerization of the semi-flexible macromolecules ($L_i = 1$ in the case of simple liquids) and their rigidity is expressed by the persistence length q , which is a measure of how far a polymeric chain persists in a given direction [16]. In the elastic chain model [13, 17], q is related to the elastic energy κ of the chain by the relation $q = 2\beta\kappa$ (with $\beta = 1/k_B T$, k_B being the Boltzmann constant).

The coefficients A, B, C, D take into account the effects of temperature and rigidity.

We recover, in the first part of this expression, a Flory type free energy [18] describing a non-mesomorphic mixture, χ being the Flory mean interaction parameter (repulsive).

The phenomenological dynamical equations describing the time evolutions of the two order parameters are of the Ginzburg–Landau type (non-conservative order parameter S) and the Cahn–Hilliard type (conservative order parameter ϕ), respectively [4, 19]

$$\frac{dS}{dt} = -\gamma \frac{\delta \mathcal{F}}{\delta S} \quad (3)$$

and

$$\frac{d\phi}{dt} = M \nabla^2 \frac{\delta \mathcal{F}}{\delta \phi}. \quad (4)$$

The sample is taken to be sufficiently thin in the \hat{z} direction to assume that the order parameters are constant along this direction. Then, in the case when $\hat{n} \parallel \hat{z}$ ($K_3 = 0$ corresponding to a homeotropic anchorage of the molecules), we have

$$\frac{\delta \mathcal{F}}{\delta S} = \frac{\partial f}{\partial S} - K_2 \phi \nabla^2(\phi S) \quad (5)$$

and

$$\frac{\delta \mathcal{F}}{\delta \phi} = \frac{\partial f}{\partial \phi} - K_1 \nabla^2(S) - K_2 S \nabla^2(\phi S). \quad (6)$$

The coefficients M and γ are, respectively, related to the translational and rotational mobilities and are positive.

In a following section, we will show, through a numerical example, the influence of a planar anchorage (then, \hat{n} is in the plane of variations of ϕ and S) of the director on the phase separation processes.

2.2. Short time behaviour of the phase separation

The system, prepared at a temperature at which it is in a homogeneous phase for all possible concentrations, is quenched at a fixed temperature, inside the demixing region. We suppose that it remains in the same orientational state when it is taken up to the experiment temperature. We study the stability of the mixture with respect to small fluctuations of the order parameters, around their mean values.

The homogeneous state is described by a pair of values (ϕ_0, S_0) and we define the associated infinitesimal fluctuations $(\delta\phi, \delta S)$ by

$$\phi = \phi_0 + \delta\phi \quad (7)$$

and

$$S = S_0 + \delta S, \quad (8)$$

and with $\delta\phi \ll \phi_0$ and $\delta S \ll S_0$.

A limited expansion of the free energy density $f(\phi, S)$ around (ϕ_0, S_0) leads to

$$\begin{aligned} \frac{\partial f}{\partial \phi} &= \left(\frac{\partial f}{\partial \phi} \right)_{\phi_0, S_0} + \delta\phi \left(\frac{\partial^2 f}{\partial \phi^2} \right)_{\phi_0, S_0} \\ &+ \delta S \left(\frac{\partial^2 f}{\partial \phi \partial S} \right)_{\phi_0, S_0} + \dots \end{aligned} \quad (9)$$

$$\begin{aligned} \frac{\partial f}{\partial S} &= \left(\frac{\partial f}{\partial S} \right)_{\phi_0, S_0} + \delta S \left(\frac{\partial^2 f}{\partial S^2} \right)_{\phi_0, S_0} \\ &+ \delta\phi \left(\frac{\partial^2 f}{\partial \phi \partial S} \right)_{\phi_0, S_0} + \dots, \end{aligned} \quad (10)$$

with

$$\left(\frac{\partial f}{\partial \phi} \right)_{\phi_0, S_0} = \text{Cste} \quad (11)$$

and

$$\left(\frac{\partial f}{\partial S} \right)_{\phi_0, S_0} = 0 \quad (12)$$

Equation (12) determines the value of the orientational order parameter S_0 , for a given mean concentration ϕ_0 and a fixed temperature.

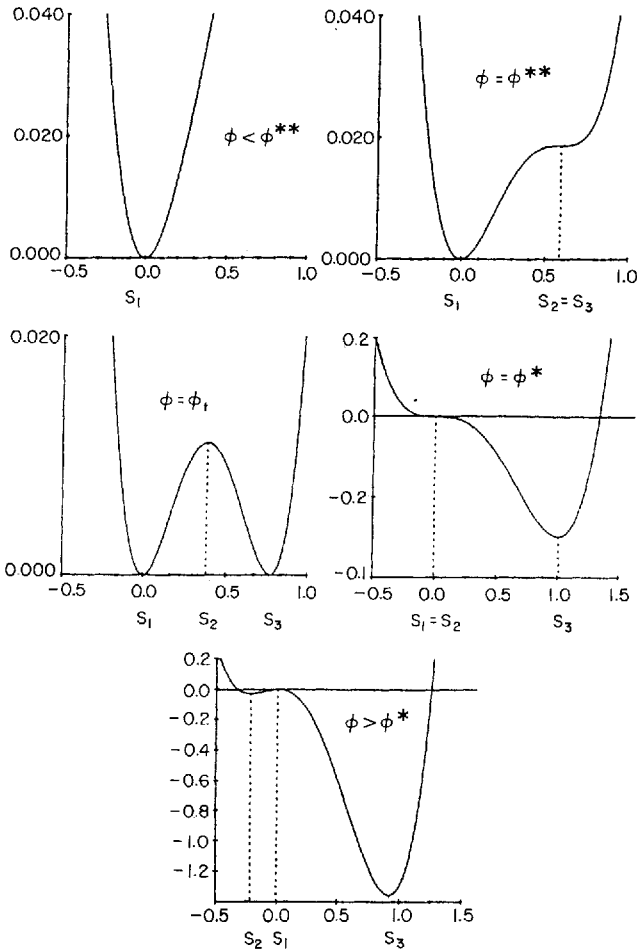


Figure 1. Variation of the free energy density as a function of S , the orientational order parameter, at a fixed temperature and various concentrations.

Taking into account the shape of the free energy density (expression (2)), one can find three extreme situations (see figure 1) with respect to S

$$S_1 = 0, \tag{13}$$

$$S_2 = \frac{3B}{8C\phi_0} \left(1 - \sqrt{1 - \frac{32C(A\phi_0 + D)}{9B^2\phi_0}} \right), \tag{14}$$

and

$$S_3 = \frac{3B}{8C\phi_0} \left(1 + \sqrt{1 - \frac{32C(A\phi_0 + D)}{9B^2\phi_0}} \right). \tag{15}$$

We must note that we work on a free energy density surface $f(\phi, S)$ and as we choose an equilibrium initial state, the concentration ϕ_0 is correlated to the orientational order parameter S_0 which minimizes the free energy density (equations (13), (14), (15)). Then, to give some idea of the dynamical behaviour of the system, it is helpful to visualize the free energy curve corresponding

to these solutions. Quite simple trends can be obtained through this representation.

Then, we choose, for temperatures at which the phase separation proceeds, the S_0 value corresponding to the absolute minimum of the free energy density (see figure 1); that means $S_0 = S_1$ if $\phi < \phi_t$ (isotropic states) and $S_0 = S_3$ if $\phi > \phi_t$ (anisotropic states) (see figures 2 and 3).

$[\phi_1^i, \phi_2^i]$, $[\phi_1, \phi_2]$ correspond to the binodal limits respectively, of the isotropic–isotropic and isotropic–anisotropic phase separations. ϕ_s is the inflection point (‘spinodal point’) of the anisotropic branch. At ϕ_t , there

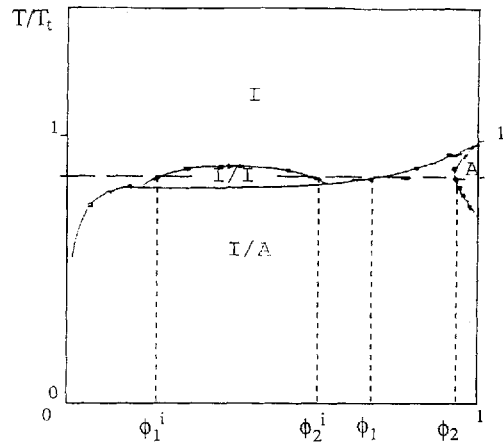


Figure 2. Example of the phase diagram for a mesomorphic (A) / non-mesomorphic (B) mixture calculated from mean field theory [15] with $L_A/q_A = 2.5$, $L_A/L_B = 2.5$ and $\chi L_A(T_i) = 3$ (I and A are, respectively, the homogeneous isotropic and anisotropic phases; I/I and I/A are respectively the isotropic–isotropic and isotropic–anisotropic biphasic).

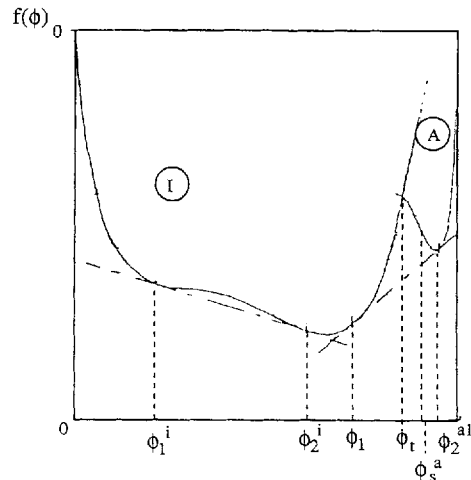


Figure 3. Example of the free energy density at $T/T_t = 0.85$ (horizontal dashed line on figure 2; I and A are respectively the isotropic and anisotropic branches of the free energy density).

exists an equal probability of finding the mesomorphic compound in an isotropic or an anisotropic state.

In Fourier space, the linearized equations (3) and (4) lead to

$$\frac{d}{dt} \begin{pmatrix} \delta\phi \\ \delta S \end{pmatrix} = - \begin{pmatrix} Mk^2 & 0 \\ 0 & \gamma \end{pmatrix} \times \begin{pmatrix} \alpha_{11} + k^2(K_1 + K_2 S_0^2) & \alpha_{12} + K_2 k^2 S_0 \phi_0 \\ \alpha_{12} + K_2 k^2 S_0 \phi_0 & \alpha_{22} + k^2 K_2 \phi_0^2 \end{pmatrix} \times \begin{pmatrix} \delta\phi \\ \delta S \end{pmatrix} \quad (16)$$

$$= -LA \begin{pmatrix} \delta\phi \\ \delta S \end{pmatrix}, \quad (17)$$

with

$$\alpha_{11} = \left(\frac{\partial^2 f}{\partial \phi^2} \right)_{\phi_0, S_0}, \quad \alpha_{22} = \left(\frac{\partial^2 f}{\partial S^2} \right)_{\phi_0, S_0}, \quad (18)$$

$$\alpha_{12} = \left(\frac{\partial^2 f}{\partial \phi \partial S} \right)_{\phi_0, S_0},$$

where, using the free energy density (2), α_{11} , α_{22} and α_{12} are functions of ϕ_0 , S_0 and the derivative of S with respect to ϕ taken at the point (ϕ_0, S_0) .

The system, prepared at (ϕ_0, S_0) , is stable with respect to infinitesimal perturbations only if all the eigen values of the linear matrix (LA) are positive, and unstable if at least one eigen value is negative. Then, the boundary of the instability zone is given by the couples (ϕ_0, S_0) which verify $\det(LA) = 0$.

We neglect, in a first step, the term related to the spatial variations of the order parameters, for example, $K_1 = K_2 = 0$.

Then, the boundary of the instability is

$$\gamma Mk^2 (\alpha_{11} \alpha_{22} - \alpha_{12}^2) = 0 \quad (19)$$

and we note $\mathcal{C}_T = \alpha_{11} \alpha_{22} - \alpha_{12}^2$, the total curvature of the free energy density surface. Then, the pair of initial values (ϕ_0, S_0) driving the system to an unstable state confirms $\mathcal{C}_T \leq 0$.

In the special case when the mixture is prepared at high temperature, in the isotropic phase, and quenched to a lower temperature at which a phase separation can occur, $S(\phi) = S_1 = 0$. Then we have

$$\left. \begin{aligned} \alpha_{11} &= \frac{1}{L_A \phi_0} + \frac{1}{L_B (1 - \phi_0)} - 2\chi, \\ \alpha_{22} &= \frac{2}{L_A} (A \phi_0^3 + D \phi_0^2), \\ \alpha_{12} &= 0, \end{aligned} \right\} \quad (20)$$

and, with the help of the expressions (20) and the hypothesis $K_1 = K_2 = 0$, the linearized system of equations

is rewritten

$$\frac{d}{dt} \begin{pmatrix} \delta\phi \\ \delta S \end{pmatrix} = - \begin{pmatrix} Mk^2 \alpha_{11} & 0 \\ 0 & \gamma \alpha_{22} \end{pmatrix} \begin{pmatrix} \delta\phi \\ \delta S \end{pmatrix} \quad (21)$$

$$\Leftrightarrow \begin{cases} \delta\phi = \delta\phi_0 \exp(-Mk^2 \alpha_{11} t) \\ \delta S = \delta S_0 \exp(-\gamma \alpha_{22} t) \end{cases} \quad (22)$$

where $\delta\phi_0$, δS_0 are the initial infinitesimal perturbations of the order parameters around ϕ_0 , S_0 at $t = 0$.

The instability zone verifies $\alpha_{11} \alpha_{22} < 0$ and we note that the evolution of each of the two order parameters is independent (diagonal system, equation (22)). We can determine the short time behaviour of the system with the help of the generic case of a mesomorphic/non-mesomorphic binary mixture; the system is initially prepared at the reduced temperature T_0/T_i (where T_i is the pseudo-transition temperature of the single mesomorphic component) and quenched to the temperature T_1/T_i (see figures 2 and 3).

Various cases must be taken into account as a function of the initial mean concentration ϕ_0 , but, in all cases $\alpha_{11} > 0$, since S_0 implies that ϕ_0 is on the isotropic branch of the free energy density (with respect to ϕ).

In the following, ϕ^{**} is the concentration below which the system is in an isotropic phase and ϕ^* the concentration above which the system is in an anisotropic phase (figure 1).

$\phi_0 < \phi^{**}$: The α_{22} curvature of the free energy density with respect to S is positive; then, from equations (22), the orientational perturbations must decrease (isotropic state).

The α_{11} curvature of the free energy density is negative only if the concentration ϕ is in the isotropic–isotropic spinodal zone: then, the system is unstable with respect to small fluctuations of ϕ and an isotropic–isotropic phase separation can occur with a spinodal decomposition dynamical process (Cahn–Hilliard) [20].

$\phi_0 > \phi^{**}$: We have two sub-cases, according to whether the mean concentration ϕ_0 is lower or greater than ϕ^* (see figure 1):

- if $\phi^{**} < \phi_0 < \phi^*$: the system is on the isotropic branch of the free energy density with respect to ϕ and S , and then α_{11}, α_{22} are positive at the point $(\phi_0, S_0 = 0)$. From (22), we note that the two order parameter fluctuations decrease, keeping the system in an isotropic phase (in fact it is a metastable state which cannot be described by such a perturbative theory).
- if $\phi_0 > \phi^*$: α_{11} is always positive, but α_{22} becomes negative. Then, we are in a zone in which the orientational order parameter fluctuations must increase (equation (22)).

This exponential growth during the first stages of the transition saturates in the next stages by the non-linear

terms (equation (3)), which leads the mixture into a new orientational state $S'_0 = S_2 \neq 0$, minimizing the free energy density solution of

$$\left(\frac{\partial f}{\partial S}\right)_{\phi_0, S_0} = 0 \Leftrightarrow S'_0 = S_3$$

$$= \frac{3B}{8C\phi_0} \left(1 + \sqrt{\left[1 - \frac{32C(A\phi_0 + D)}{9B^2\phi_0}\right]}\right), \quad (23)$$

where S_3 is the absolute minimum of the free energy density with $\phi = \phi_0$ (see figure 1).

Then, after the first instability, the mixture reaches an anisotropic, homogenous state (ϕ_0, S'_0) and we can again study the instability conditions of the system with respect to small perturbations. We should remember that S'_0 is a minimum of the free energy, which implies that α_{22} is always positive.

The boundaries of the instability zone, defined by $\mathcal{C}_T < 0$, can be obtained through α_{11} negative.

Then, we recover a case analogous to the non-mesomorphic mixture, which means that the system, in a spinodal zone, becomes unstable (negative curvature with respect to ϕ of the free energy density).

We can study the wavelength of textures appearing in the system during the first stages of the isotropic-anisotropic phase separation, by taking into account the spatial variation terms.

We calculate the eigen values ω of the linear matrix (LA) which verifies (lengths are normalized by $\sqrt{K_2}$: $x \rightarrow K_2^{1/2}x$)

$$\omega^2 - B(k)\omega + C(k) = 0 \Leftrightarrow \omega_{\pm} = \frac{B(k) \pm \sqrt{B^2 - 4C}}{2}, \quad (24)$$

with

$$\left. \begin{aligned} B(k) &= b_2k^4 + b_1k^2 + b_0, \\ C(k) &= c_2k^6 + c_1k^4 + c_0k^2 \end{aligned} \right\} \quad (25)$$

where

$$\left. \begin{aligned} b_2 &= (K_1/K_2 + S_0^2)(M/K_2), \\ b_1 &= (M/K_2)\alpha_{11} + \gamma\phi_0^2, \\ b_0 &= \gamma\alpha_{22}, \\ c_2 &= \gamma M(K_1/K_2^2)\phi_0^2, \\ c_1 &= \gamma(M/K_2)\eta, \\ c_0 &= \gamma(M/K_2)\mathcal{C}_T, \\ \eta &= \alpha_{11}\phi_0^2 + \alpha_{22}(K_1/K_2 + S_0^2) - 2\alpha_{12}\phi_0S_0. \end{aligned} \right\} \quad (26)$$

For reasons of simplicity, we have substituted S'_0 by S_0 .

Being interested in the first stages of the separation, we have very different evolution laws for the two order

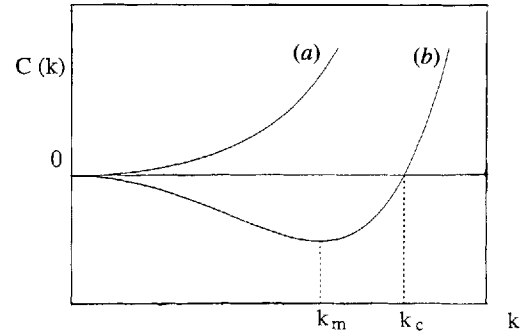


Figure 4. $C(k)$ as function of various parameters of the system: (a) $\eta > 0$ and $\mathcal{C}_T > 0$ and (b) any η and $\mathcal{C}_T < 0$.

parameters (the conservative laws are different) and we can write, to a first approximation [21]

$$\frac{Mk^2}{\gamma} \ll 1, \quad (27)$$

which simplifies the study of the eigen values. They can be rewritten to the first order in MK^2/γ

$$\left. \begin{aligned} \omega_+ &= 2\left(\gamma a_0 - Mk^2\left(\frac{a_1}{a_0} - a_2\right)\right), \\ \omega_- &= 2Mk^2\frac{a_1}{a_0}, \end{aligned} \right\} \quad (28)$$

with

$$\left. \begin{aligned} a_0 &= k^2\phi_0^2 + \alpha_{22}, \\ a_1 &= \frac{K_1}{K_2}\phi_0^2k^4 + \frac{\eta}{K_2}k^2 + \frac{\mathcal{C}_T}{K_2}, \\ a_2 &= \frac{1}{K_2}\left(\frac{K_1}{K_2} + S_0^2\right)k^2 + \frac{\alpha_{11}}{K_2}. \end{aligned} \right\} \quad (29)$$

ω_+ is always positive since $\omega_+(k=0) = 2\gamma\alpha_{22} > 0$ (orientational order parameter hypothesis) and the wavevectors k solutions, leading to $\omega_+ = 0$, verify

$$\omega_+ = 0 \Leftrightarrow \gamma K_2(\phi_0^2k^2 + \alpha_{22})^2 + Mk^2(\phi_0S_0k^2 + \alpha_{12})^2 = 0, \quad (30)$$

which has no real solutions.

Then, the only eigen value which can become negative as a function of k is ω_- . As a function of $C(k)$, ω_- can be rewritten

$$\omega_- = \frac{2}{\gamma} \frac{C(k)}{(\phi_0^2k^2 + \alpha_{22})}. \quad (31)$$

The wavevectors leading to a negative ω_- are then the same as those giving $C(k)$ negative (see figure 4) (we note that, since the various coefficients are related, a total positive curvature \mathcal{C}_T imposes a positive coefficient η).

(i) $\eta > 0, \mathcal{C}_T > 0 \Rightarrow C(k) > 0 \forall k$

ω_- is positive and then, the system never becomes unstable with respect to small fluctuations: the pairs

(ϕ_0, S_0) taken such that $\mathcal{C}_T > 0$ corresponds to stable or metastable ($\alpha_{11} > 0$) zones of the free energy density, verify $\partial f / \partial S = 0$ on the free energy surface.

(ii) $\eta > 0$ or $\eta < 0 \mathcal{C}_T < 0 \Rightarrow C(k) < 0$ for $k \in]0, k_c[$.

The wavevectors k_c and k_m , corresponding, respectively, to the instability boundary limits and to the wavevector minimizing ω_- , are defined by

$$k_c = \sqrt{\left(-\frac{d_0}{2} \left[1 - \frac{|\eta|}{\eta} \sqrt{1 - 4d_1} \right] \right)} \quad (32)$$

and

$$k_m = \sqrt{\left(-\frac{d_0}{3} \left[1 - \frac{|\eta|}{\eta} \sqrt{1 - 3d_1} \right] \right)}, \quad (33)$$

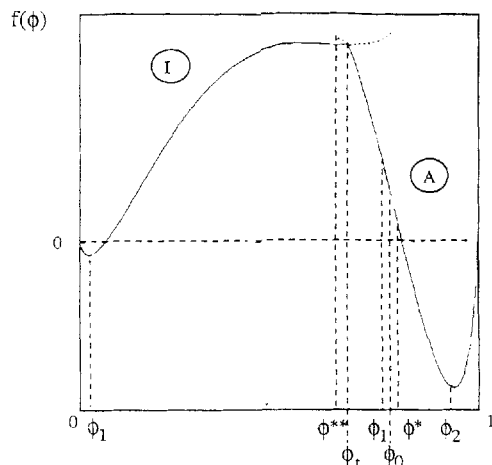


Figure 5. Free energy density at $T/T_i = 0.67$ for a binary mixture of a rod-like mesomorphic component ($L_A = 4$) and a solvent ($L_B = 1$).

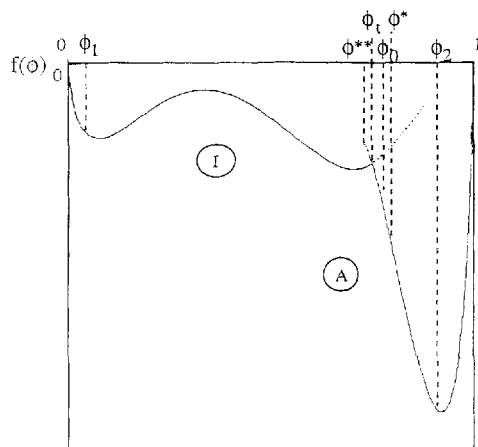


Figure 6. Free energy density at $T/T_i = 0.8$ for the same binary mixture as that in figure 5.

with

$$d_0 = \frac{c_1}{c_2} = \frac{K_2}{K_1} \frac{\eta}{\phi_0^2} \quad (34)$$

and

$$d_1 = \frac{c_0 c_2}{c_1^2} = \frac{K_1}{K_2} \frac{\mathcal{C}_T \phi_0^2}{\eta^2}. \quad (35)$$

Then, the system is unstable with respect to small fluctuations when prepared at mean concentration-orientational order parameter pairs (ϕ_0, S_0) such that $\alpha_{11} < 0$ and the mean lengths of the nucleating zones are of the order of $1/k_m$ during the first stages of the separation, the orientational order parameter being then a slave to the variations of concentration [22].

3. Numerical simulations

The numerical solutions of the system of coupled non-linear partial derivative equations (1) is realized on a square grid 128×128 , on a parallel supercomputer (Connection Machine CM-200), using an explicit finite difference scheme. The colour palette used is chosen such that the lower colour (yellow) corresponds to $S = -0.5$ and $\phi = 0$ and the higher colour (white) to $S = 1$ and $\phi = 1$.

We present here a few examples which describe the phase separation in a binary mixture composed of mesomorphic rod-like molecules ($L_A = 4$) and a non-

Figure 7. Time evolution of the concentration in a mesomorphic/non-mesomorphic binary mixture (parameters of figure 5) at $T/T_i = 0.67$ and $\phi_0 = 0.78$. From left to right, from top to bottom: $t = 0, 150, 221, 371, 577, 1601, 1921, 2544, 3316, 4636, 6889, 17607, 125506, 187885, 686647, 863042$ (expressed in time step unit $\delta t = 0.01$).

Figure 8. Time evolution of the orientational order parameter in the mesomorphic/non-mesomorphic mixture at $T/T_i = 0.67$ and $\phi_0 = 0.78$ at same times as in the preceding figure (the red and purple colours correspond, respectively, to isotropic and anisotropic zones).

Figure 11. Time evolution of the concentration in a mesomorphic/non-mesomorphic binary mixture (parameters of figure 5) at $T/T_i = 0.8$ and $\phi_0 \approx \phi^{**}$. From left to right, from top to bottom: $t = 0, 279, 427, 1004, 2494, 6662, 28832, 51174$ (expressed in time step unit $\delta t = 0.01$).

Figure 12. Time evolution of the orientational order parameter in the mesomorphic/non-mesomorphic mixture at $T/T_i = 0.8$ and $\phi_0 \approx \phi^{**}$ at the same times as for the concentration evolution (figure 11).

Figure 13. Anisotropic time evolutions of the concentration (upper line) and the orientational order parameter (lower line) in the binary mixture of figure 5 with $K_3 > 0$ and $\beta|\delta|$, at $T/T_i = 0.67$. From left to right: $t = 174, 1184, 2821, 4269$ ($\delta t = 0.01$).

Figure 14. The same evolutions as in figure 13, but at $T/T_i = 0.8$. From left to right: $t = 648, 4817, 16712, 76122$ ($\delta t = 0.01$).

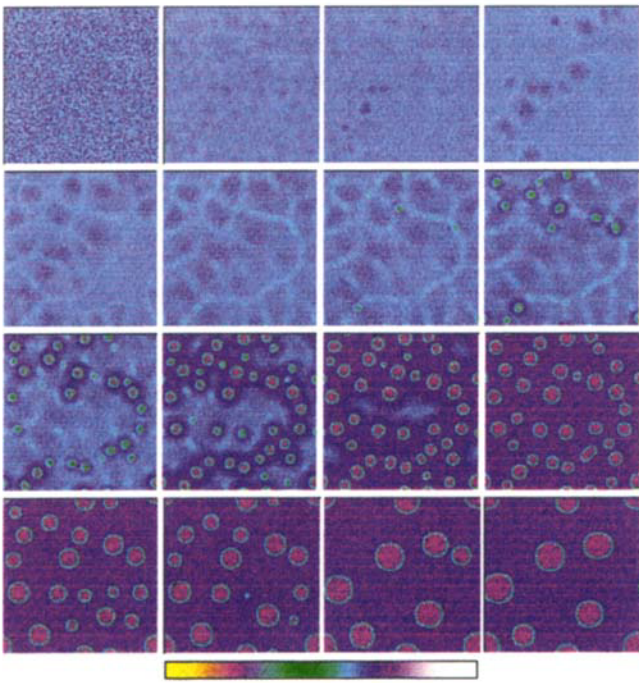


Figure 7.

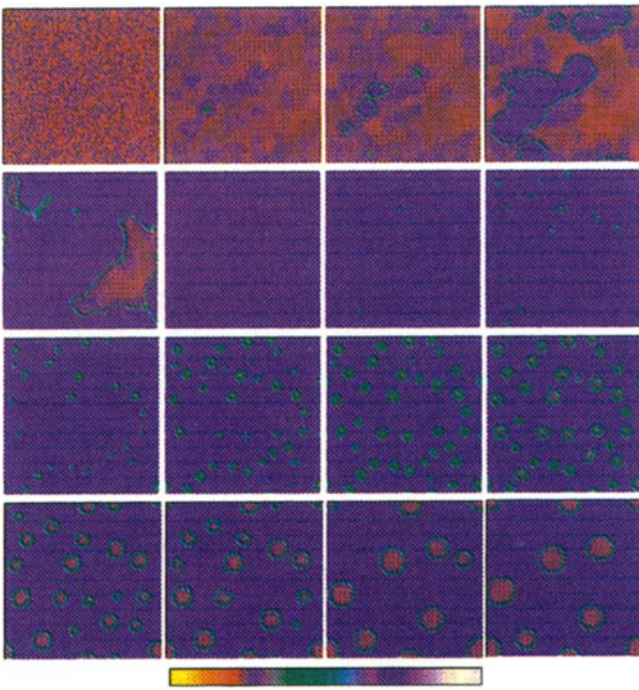


Figure 8.

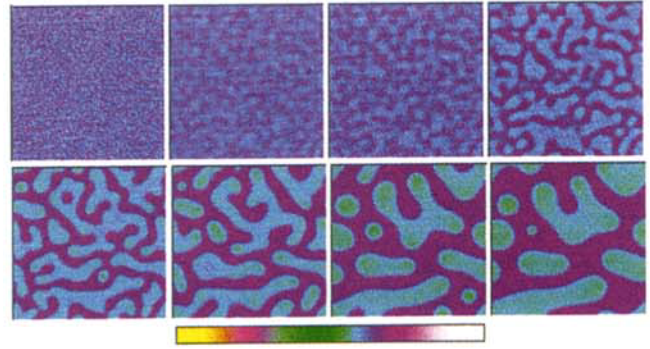


Figure 11.

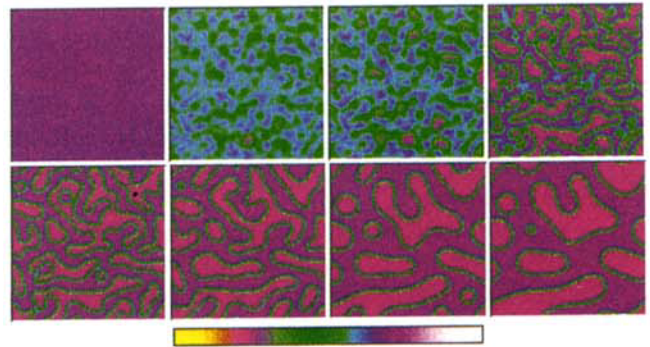


Figure 12.

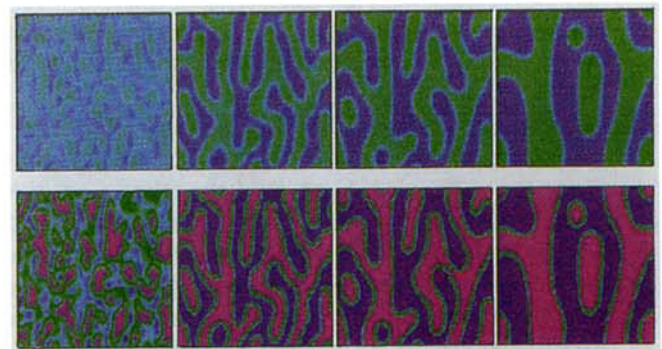
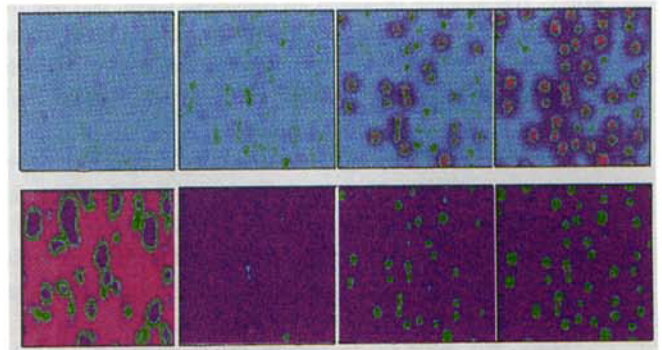


Figure 14.

mesomorphic solvent ($L_B = 1$), induced by small fluctuations of the order parameters.

In the first one, the system is initially prepared in an isotropic phase, with a mesomorphic component concentration $\phi_0 = 0.78$, and quenched to the reduced temperature $T/T_i = 0.67$. We have a homeotropic anchorage ($K_3 = 0$).

The mean concentration ϕ_0 has been chosen between $\phi^* = 0.7763$ and $\phi_s^a = 0.7919$ (see figure 5) to illustrate the phase separation processes in two stages from an unstable state. This situation has been analytically described in the preceding section.

Then, we see in figures 7, 8, 9 and 10 that the phase separation occurs in two stages: the first stage corresponds to the orientational order parameter instability (isotropic–anisotropic phase transition) at a constant concentration ϕ_0 (independent of time evolution) and the second one, to a ‘classical’ phase separation (spinodal decomposition), the concentration inducing variations of the orientational order parameter.

We verify on numerical sections of the order parameters (see figures 9 and 10) that, after the first stages governed by the time variations of S , the evolutions of the two order parameters are strongly correlated, the orientational order parameter being, in the later stages, a slave of the concentration variations.

We must note in this first example, that, after the first stage, the system reached an unstable state, but the phase separation patterns are not interconnected zones, because, the concentration being a conservative order parameter, these textures appear only when $\phi_0 \approx (\phi_1 + \phi_2)/2$ (where ϕ_1 and ϕ_2 are the binodal points).

In the second example, we initially prepare the system at a concentration ϕ^{**} (see figure 6) in a homogeneous stable anisotropic phase (homeotropic anchorage) and quench it to a reduced temperature $T/T_i = 0.8$, at which it is in an unstable state, both with respect to concentration ϕ and degree of orientation S (see figure 1).

Thus, the phase separation takes place by interconnected zones and the variation of the orientational order parameter is always a slave of variation in concentration. The patterns are, as in the first example, spatially isotropic, since the anchorage is homeotropic (anisotropic effects are perpendicular to the plane of variation) (see figures 11 and 12).

Then, we study the same system, at these two temperatures, with a planar anchorage, the director being along the y direction. Here, we have taken a positive K_3 value. Thus, we find again the process of phase separation in two stages ($T/T_i = 0.67$) and the pattern of interconnected areas ($T/T_i = 0.8$), but with a large anisotropy oriented in the direction of the director, as observed experimentally [6] (see figures 13 and 14).

In the case when K_3 is negative, the direction of growing

patterns is orthogonal to the director. This seems to be the case in recent small angle neutron scattering experiments made on polyester mixtures [23].

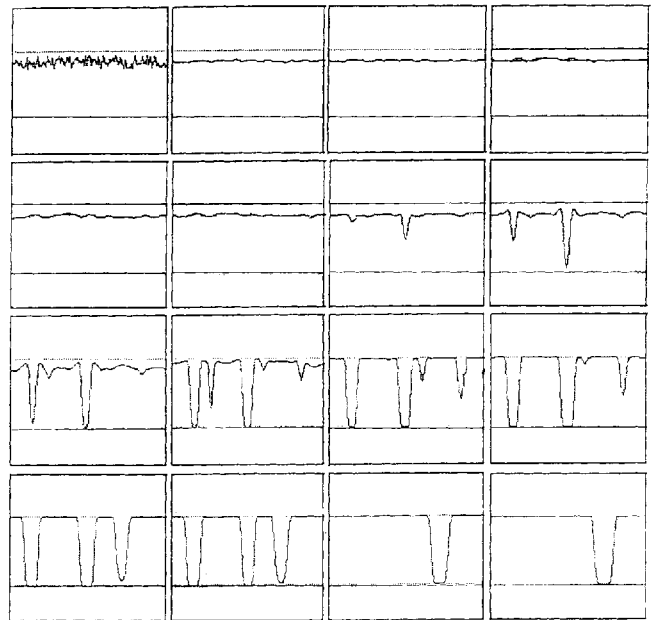


Figure 9. Time evolution of the concentration section along x for the mesomorphic/non-mesomorphic binary mixture $T/T_i = 0.67$ and $\phi_0 = 0.78$ (the horizontal lines correspond to the two binodal values).

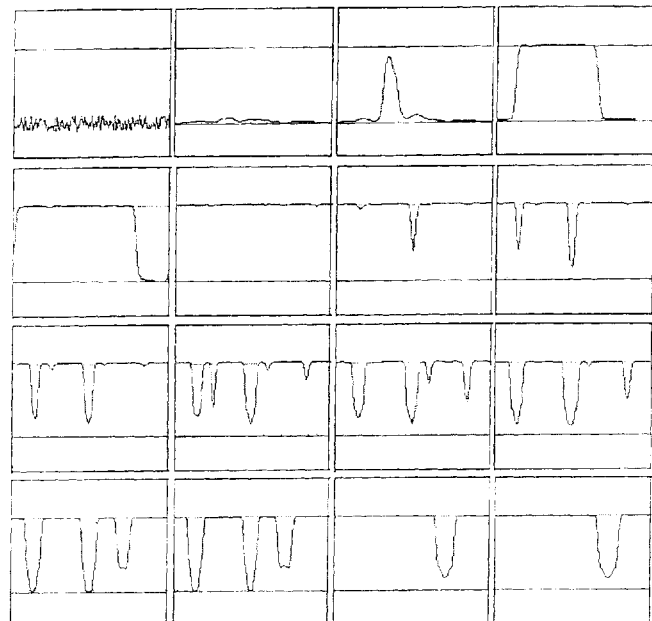


Figure 10. Time evolution of the orientational order parameter section along x for the mesomorphic/non-mesomorphic binary mixture at $T/T_i = 0.67$ and $\phi_0 = 0.78$ (the horizontal lines correspond to the isotropic $S = S_1 = 0$ and the anisotropic $S = S_3$ values).

4. Conclusions

In the present work, we have derived a coupled system of non-linear partial derivative equations in the case of a mesomorphic/non-mesomorphic binary mixture, from an expression of the functional coarse-grained free energy derived in previous work. Then we studied multiple components mixtures composed of small molecule solvent, conventional polymers or mesomorphic molecules or macromolecules.

These equations are of the Ginzburg–Landau type for the non-conservative scalar orientational order parameter and of the Cahn–Hilliard type for the conservative order parameter (the concentration of the mesomorphic species).

We have shown that in particular zones of the phase diagram (special concentrations) and during the early stages, the demixing occurs in two stages, a phase transition followed by a phase separation. During the second stage, where the orientational order parameter S is a slave of the concentration variations, we note the existence of a critical wavevector above which the phase separation cannot occur.

We illustrate the two stage behaviour of the dynamical process with the help of numerical simulations of this set of equations and we qualitatively enlighten the importance of non-linear terms at longer times.

In future work, we will quantitatively study the phase separation in mesomorphic/non-mesomorphic binary mixtures and the time evolution of the structure factor, with the help of numerical simulations, in order to make comparisons with recent small angle neutron and light scattering experiments.

We will also take into account the director variations in the system by substitution of the scalar orientational order parameter S by a tensorial one, $Q_{ij} = S/2(3n_i n_j - \delta_{ij})$ describing the coupling between S and \hat{n} [14].

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References

- [1] SAN MIGUEL, M., AMENGUAL, A., and HERNANDEZ-GARCIA, E., 1994, *Phase Transit.*, **48**, 65.
- [2] HASHIMOTO, T., 1988, *Phase Transit.*, **12**, 47.
- [3] KOMURA, S., 1988, *Phase Transit.*, **12**, 3.
- [4] GUNTON, J. D., SAN MIGUEL, M., and SAHNI, P., 1983, *Phase Transitions and Critical Phenomena* Vol. 8, edited by C. Domb and J. L. Lebowitz (Academic Press).
- [5] CASAGRANDE, C., FABRE, P., GUEDEAU, M. A., and VEYSSIE, M., 1987, *Europhysics Lett.*, **3**, 73.
- [6] CASAGRANDE, C., VEYSSIE, M., and KNOBLER, C. M., 1987, *Phys. Rev. Lett.*, **58**, 2079.
- [7] AHN, W., KIM, C. Y., and KIM, S. C., 1992, *Macromolecules*, **25**, 5002.
- [8] NAGAYA, T., ORIHARA, H., and ISHIBASHI, Y., 1989, *J. phys. Soc. Japan*, **58**, 3600.
- [9] NAKAI, A., SHIWAKU, T., HASEGAWA, H., and HASHIMOTO, T., 1986, *Macromolecules*, **19**, 3010.
- [10] ESSEY, R. L. H., and BALL, R. C., 1991, *Europhysics Lett.*, **16**, 379.
- [11] DORGAN, J. G., 1993, *J. chem. Phys.*, **98**, 9094.
- [12] SHIMADA, T., DOI, M., and OKANO, K., 1988, *J. chem. Phys.*, **88**, 7181.
- [13] LANSAC, Y., and MAISSA, P., 1992, *Physica A*, **180**, 53.
- [14] PING SHENG, and PRIESTLY, E. B., 1979, *Introduction to Liquid Crystals*, edited by E. B. Priestly, P. J. Wojtowicz and Ping Sheng. (Plenum Press).
- [15] MAISSA, P., and SIXOU, P., 1989, *Liq. Crystals*, **5**, 1861.
- [16] YAMAKAWA, H., and FUJII, M., 1973, *Macromolecules*, **6**, 407; 1974, *Ibid.*, **7**, 128.
- [17] SAITO, N., TAKAHASHI, K., and YUNOKI, Y., 1967, *J. phys. Soc. Japan*, **22**, 219.
- [18] FLORY, P. J., 1956, *Proc. R. Soc. Lond. A*, **234**, 60; 1956, *Ibid.*, **234**, 73.
- [19] HOHENBERG, P. C., and HALPERIN, B. I., 1977, *Rev. mod. Phys.*, **49**, 435.
- [20] CAHN, J. W., 1968, *Trans. Metal. Soc. AIME*, **242**, 1966.
- [21] SAN MIGUEL, M., GUNTON, J. D., DEE, G., and SAHNI, S., 1981, *Phys. Rev. B*, **23**, 2334.
- [22] DEE, G., GUNTON, J. D., and KAWASAKI, K., 1980, *Prog. theor. Phys.*, **65**, 365.
- [23] FRIED, F., LANSAC, Y., SIXOU, P., BLUMSTEIN, A., and BLUMSTEIN, R., 1990, *IUPAC Macro 90-1. 1 Blends*, Montreal, Canada.