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Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Dorgan, John R.(1991) 'Spinodal decomposition in mixtures containing nematogens', Liquid Crystals, 10: 3, 347 — 355
To link to this Article: DOI: 10.1080/02678299108026281
URL: http://dx.doi.org/10.1080/02678299108026281

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Liquid Crystals, 1991, Vol. 10, No. 3, 347–355

Spinodal decomposition in mixtures containing nematogens

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(*Received 11 September 1990; accepted 18 February 1991*)

A general stability criterion is presented for mixtures containing nematic liquid crystals. Conditions for absolute phase instability are found and represent a generalization of the usual spinodal concept. Physically, these conditions represent instabilities with respect to variations in the systems composition, degree of molecular ordering or some combination thereof. An example calculation corresponding to a liquid-crystalline polymer is presented. This calculation is based upon a well known lattice model which includes energetics that are dependent upon molecular orientation. Spinodal decomposition has profound effects on the morphology of a system which undergoes phase separation. Recent experimental and theoretical studies have attempted to explore these consequences in liquid-crystalline systems. None gives a rigorous definition of what is meant by spinodal in a mixture with orientational degrees of freedom; the material presented here clarifies this issue.

1. Introduction

The concept of the spinodal as the thermodynamic limit of phase stability is well established. The consequences regarding the morphology of a system which undergoes spinodal decomposition are profound [1]. The investigation of spinodal decomposition in mixtures containing polymeric nematic liquid crystals is of great technological importance and is the focus of recent experimental and theoretical studies [2–6]. None of these works has given a definition of the spinodal region which goes beyond calling it an unstable regime [5]. Liquid-crystalline systems are unique and the meaning of the spinodal is distinct from non-ordering systems. An exposition on the calculation and interpretation of the spinodal curve in multicomponent mixtures containing nematic liquid crystals is presented here.

Previous work concerning the thermodynamic phase stability of liquid-crystalline materials is scarce. The notable exception is the work of Stecki and Kloczkowski [7, 8]. These authors correctly identify the general criterion for phase stability. They apply this criterion to test the stability of the pure component isotropic phase with respect to nematic and smectic A ordering.

This paper presents the general stability criterion for mixtures containing both regular and nematic fluids. This criterion is shown to be a generalization of the usual spinodal concept. An example phase diagram is presented based upon a lattice theory of rod-like molecules in solution.

2. Theoretical

The analysis of phase stability begins with an expression for the appropriate thermodynamical potential. Stability of the thermodynamic system with respect to variations in composition and orientation is of interest for liquid-crystalline materials. Example calculations based on a lattice model are presented in the next section; this model does not allow for compressibility of the solution. This means the partition function yields a Helmholtz rather than a Gibbs free energy. The extension of the formalism presented here to compressible systems is straightforward. In order to develop this formalism, consider the case where the Helmholtz free energy is expressed as a function of composition and orientation

$$\frac{A}{VRT}=F\{v_{i=1,n},\ y_{j=1,m}\}. \tag{1}$$

Here, y_j represents a scalar order parameter, v_i is the volume fraction for each species present and F is a dimensionless free energy density function. The number of nematogens may be equal to or less than the total number of species present, $(m \leqslant n)$.

The conditions for absolute phase stability correspond to a minimum in the free energy of the system. At this minimum energy state any variation in the values of the independent variables must lead to an increase in the systems energy

$$\delta A \geqslant 0. \tag{2}$$

By this statement it is meant that the change in the systems energy for small changes in any components order parameter or volume fraction must be positive.

In considering the stability of the system, care must be taken to include the restraint that the number of each species present is conserved

$$\left(1-\sum_{i=1}^{n} v_i\right)=0. \tag{3}$$

This constraint is included by rewriting the free energy expression in terms of the $(n-1)$ independent volume fractions

$$\frac{A}{VRT}=F\{v_{i=1,(n-1)},\ y_{j=1,m}\}. \tag{4}$$

This guarantees that no inadmissible variations in composition are considered in the analysis.

Examination of the change in the free energy when a fluctuation occurs within the fixed system volume, V, forms the basis of the stability analysis. Consider the change in the systems intensive free energy caused when the values of v_i and y_j fluctuate by a small amount. This may be expressed in the form of a Taylor series expansion about the homogeneous equilibrium state by

$$\begin{aligned}\delta F=&\left(\frac{\partial F}{\partial v_i}\right)\delta v_i+\left(\frac{\partial F}{\partial y_j}\right)\delta y_j\\&+\frac{1}{2}\left\{\left(\frac{\partial^2 F}{\partial v_i \partial v_k}\right)(\delta v_i \delta v_k)+\left(\frac{\partial^2 F}{\partial y_j \partial y_l}\right)(\delta y_j \delta y_l)+\left(\frac{\partial^2 F}{\partial v_i \partial y_j}\right)(\delta v_i \delta y_j)\right\}+\dots\end{aligned} \tag{5}$$

The derivatives are evaluated at the uniform equilibrium conditions. All terms are implied by the summation convention. The variations are arbitrary; they may be either positive or negative. The first order terms must vanish in light of condition (2).

Stability of the equilibrium state is ensured when the second order terms are positive for arbitrary variations in the independent variables [9]. Likewise, the system is absolutely unstable if the second order terms are negative for such variations. This is the condition invoked by Stecki and Kloczkowski in studying the stability of the pure component isotropic phase of a nematogen [8]. This is also the general criterion used for compressible solutions [10]. As already demonstrated, the expansion of the free energy about an equilibrium state takes the form of a Taylor series. The second order terms in this expansion (the second variation) take the form

$$\delta_2 = \frac{1}{2}\left(\frac{\partial^2 F}{\partial u_i \partial u_j}\right)\delta u_i \delta u_j, \tag{6}$$

where u_i and u_j are dummy variables representing the independent volume fractions and the order parameters for the species contained in the mixture.

The main result presented here is the conditions under which the equilibrium state becomes absolutely unstable. This means that the systems free energy can be lowered by an infinitesimal variation in one or more of its independent arguments. The second variation may be written as

$$\delta_2 = \tfrac{1}{2} E_{ij} \delta u_i \delta u_j, \tag{7}$$

where the matrix of all second derivatives, E_{ij}, has been introduced. Examination of the stability criterion when one field variable is varied while all others are held constant results in

$$E_{ii}(\delta u_i)^2 > 0. \tag{8}$$

Therefore, a conclusion of this analysis is that stability requires that all second derivatives of the intensive free energy with respect to a single independent argument be positive. However, this condition is not the most general restriction.

The matrix E_{ij} is symmetric and may therefore be diagonalized via an expansion in terms of its eigenvectors. The eigenvectors are defined according to equation (9) for each associated eigenvalue λ^k. In this and the following, subscripts k and l refer to the diagonalized form while i and j refer to the original form where

$$E_{kl} \delta u_l = \lambda^k \delta u_k, \tag{9 a}$$

and

$$\delta u_l = \delta u_k. \tag{9 b}$$

The basis vectors of the bilinear form defined by equation (7) may be expanded in terms of the eigenvectors where

$$\delta u_i = \alpha_{ik} \delta u_k, \tag{10 a}$$

and

$$\delta u_j = \alpha_{jl} \delta u_l. \tag{10 b}$$

The values of α are transformation matrices from the old basis to the new basis corresponding to the eigenvectors.

Substitution of (10) into (7) leaves the following relationship

$$\delta_2 = E_{ij} \delta u_i \delta u_j = \alpha_{ik} \alpha_{jl} E_{ij} \delta u_k \delta u_l. \tag{11}$$

The product of the first three terms on the right hand side of equation (11) represent the transformation of E_{ij} to the eigenvector basis [11] by

$$E_{kl} = \alpha_{ik} \alpha_{jl} E_{ij}. \tag{12}$$

Making use of the definition of the eigenvectors in equation (9) after substitution of (12) into (11) leads to the equality

$$\delta_2 = E_{ij}\delta u_i \delta u_j = \lambda(\delta u_k)^2. \tag{13}$$

Thus, the sign of the second variation is governed by the sign of the eigenvalues of the matrix of second derivatives; thermodynamic phase stability requires that all eigenvalues of the matrix be positive. Each eigenvalue is associated with a corresponding eigenvector. If any eigenvalue is negative, the system is absolutely unstable with respect to variations in the associated eigenvector. The eigenvalues are real and the determinant of E_{ij} is given by the product of these eigenvalues. Thus the stability criterion may be stated succinctly as, **det**$(E_{ij})>0$. It is to be noted that if the second variation vanishes, higher order terms in the expansion must be examined in order to determine the stability of the system.

To fix, ideas, consider a binary mixture composed of a nematogen and a non-nematogen. The free energy function follows according to equation (1) by

$$\frac{A}{VRT} = F\{v_{i=1,2}, y_{j=1}\}. \tag{14}$$

To make a connection with the usual spinodal concept, consider the restriction (8) when the independent quantity being varied is the independent volume fraction v_1, stability requires

$$\left(\frac{\partial^2 F}{\partial v_1^2}\right) > 0. \tag{15}$$

The system is absolutely unstable when

$$\left(\frac{\partial^2 F}{\partial v_1^2}\right) < 0, \tag{16}$$

which is just the usual definition of the spinodal region for a binary mixture [1].

The general stability of the binary mixture is governed by the eigenvalues of the derivative matrix

$$E_{ij} = \begin{bmatrix} \left(\dfrac{\partial^2 F}{\partial v_1^2}\right) & \left(\dfrac{\partial^2 F}{\partial v_1 \partial y_1}\right) \\ \left(\dfrac{\partial^2 F}{\partial y_1 \partial v_1}\right) & \left(\dfrac{\partial^2 F}{\partial y_1^2}\right) \end{bmatrix}. \tag{17}$$

For an $n \times n$ matrix, an nth order polynomial must be solved in order to find the n eigenvalues. In this case the solutions to the quadratic equation are given by [12]

$$\lambda_1 = \tfrac{1}{2}(E_{11}+E_{22}) + [\tfrac{1}{4}(E_{11}-E_{22})^2 + (E_{12})^2]^{1/2}, \tag{18a}$$

and

$$\lambda_2 = \tfrac{1}{2}(E_{11}+E_{22}) - [\tfrac{1}{4}(E_{11}-E_{22})^2 + (E_{12})^2]^{1/2}. \tag{18b}$$

Here, subscripts denote the row and column of the matrix. It is evident that the condition of positive second derivatives with respect to both independent arguments is not sufficient to ensure phase stability. Using the determinant condition the stability requirements for this example binary system may be expressed by the following inequalities:

$$\left(\frac{\partial^2 F}{\partial v_1^2}\right)\left(\frac{\partial^2 F}{\partial y_1^2}\right)-\left(\frac{\partial^2 F}{\partial v_1 \partial y_1}\right)^2 > 0, \tag{19a}$$

and

$$\left(\frac{\partial^2 F}{\partial v_1^2}\right) > 0. \tag{19b}$$

The second inequality ensures that the positive determinant does not result from the existence of two degenerate negative eigenvalues. If either of these conditions are not met the system is absolutely unstable, it is then within the spinodal region.

3. Calculations

The well known lattice theory of Flory, as modified to include free volume and anisotropic energetics [13], may be put into the functional form of equation (1). This transformation is accomplished through the use of an approximation introduced by Marrucci and Ciferra [14] along with the original Flory approximation for the distribution function [15]. The resulting expression for the extensive free energy is given by

$$\begin{aligned}\frac{A}{RT}= &-(n_0-n_r x_r+n_r y)\ln\left[1-\frac{n_r x_r}{n_0}\left(1-\frac{y}{x_r}\right)\right]+n_r\ln\left(\frac{n_r}{n_0}\right)+n_s\ln\left(\frac{n_s}{n_0}\right)+n_s(x_s-1)\\ &+n_r(y-1)+(n_0-n_r x_r-n_s x_s)\ln\left[\frac{(n_0-n_r x_r-n_s x_s)}{n_0}\right]-n_r\ln(x_r y^2)\\ &-\frac{(n_r x_r)^2}{2n_0\theta}\left(\frac{\tilde{V}_r}{\tilde{V}}\right)\left[1-\frac{3}{2}\left(\frac{\pi y}{4x_r}\right)^2\right]^2+\chi n_s x_s\left(\frac{n_r x_r \tilde{V}_r}{n_0}\right),\end{aligned} \tag{20}$$

where θ is the reduced temperature, $\tilde{V}$ represents the reduced volume of the mixture, y is the Flory order parameter and χ is an interaction parameter. Division by the total number of lattice sites, n_0, gives the intensive free energy density.

Differentiation of the extensive free energy with respect to the number of rod-like molecules, n_r, and solvent molecules, n_s, yields expressions for the chemical potentials. Letting primed quantities represent those in an anisotropic phase, this procedure gives for the rod-like molecule

$$\begin{aligned}\Delta\mu_r'/RT= &\ln\frac{v_r'}{x_r\tilde{V}_r}+v_r'(y-1)+v_s' x_r\left(1-\frac{\tilde{V}_r}{\tilde{V}_s x_s}\right)+x_r\left(\frac{\tilde{V}_r}{\tilde{V}'}-1\right)\\ &+x_r(\tilde{V}_r-1)\left[a+\ln\left(1-\frac{1}{\tilde{V}'}\right)\right]-\ln(x_r y^2)+ya+\chi v_s'^2\frac{\tilde{V}_r x_r}{\tilde{V}_s}\\ &-\frac{1}{2}\left(\frac{x_r\tilde{V}_r}{\tilde{V}'\theta}\right)\left(2\frac{v_r}{\tilde{V}_r}-(2\tilde{V}_r-\tilde{V}')\left(\frac{v_r'}{\tilde{V}_r}\right)^2\right)\left[1-\frac{3}{2}\left(\frac{\pi y}{4x_r}\right)^2\right]^2,\end{aligned} \tag{21}$$

while for the solvent molecule one obtains

$$\Delta\mu_s'/RT = \ln\frac{v_s'}{x_s\tilde{V}_s} + v_r'\frac{\tilde{V}_s x_s}{\tilde{V}_r x_r}(y-1) + v_s'\left(\frac{\tilde{V}_s}{\tilde{V}_r}x_s - 1\right)$$
$$+ x_s\tilde{V}_s\left(\frac{1}{\tilde{V}'} - \frac{1}{\tilde{V}_r}\right) + \tilde{V}_s x_s a + x_s(\tilde{V}_s - 1)\ln\left(1 - \frac{1}{\tilde{V}'}\right) + \chi x_s v_r'^2$$
$$+ \left(\frac{x_r v_r'^2}{2\theta\tilde{V}_r}\right)\left(2\frac{\tilde{V}_s}{\tilde{V}'} + 1\right)\left[1 - \frac{3}{2}\left(\frac{\pi y}{4x_r}\right)^2\right]^2, \qquad (22)$$

where use is made of the following definitions for the mixtures reduced volume and the quantity a given by

$$\frac{1}{\tilde{V}'} = \left(\frac{v_s'}{\tilde{V}_s} + \frac{v_r'}{\tilde{V}_r}\right),$$

and

$$a = -\ln\left[1 - \frac{v_r'}{\tilde{V}_r}\left(1 - \frac{y}{x_r}\right)\right].$$

Differentiation of either the extensive or intensive free energy with respect to the order parameter gives the following expression which may be solved to find the equilibrium value for y

$$-\ln\left[1 - \frac{v_r'}{\tilde{V}_r}\left(1 - \frac{y}{x_r}\right)\right] - \frac{2}{x_r} + 3\left(\frac{v_r'}{x_r\tilde{V}}\right)\left(\frac{\pi}{4}\right)^2\left(\frac{y}{\theta}\right)\left[1 - \frac{3}{2}\left(\frac{\pi y}{4x_r}\right)\right]^2 = 0. \qquad (23)$$

This equation has two solutions; the lower value of y is substituted into the derived expressions for the chemical potentials to calculate values corresponding to an anisotropic (nematic) phase. For the isotropic phase, the substitution $y = x_r$ is required [15, 16].

Using the conditions, $\Delta\mu_i = \Delta\mu_i'$, where the prime again denotes an anisotropic phase, biphasic equilibrium conditions may be found. For this example calculation, the parameter values correspond to a liquid-crystalline polymer and are given in the caption of figure 1. The calculation proceeds by fixing the temperature and assuming values for v_r' and v_r. The order parameter, y, is found from equation (23). Using this value for y in the expression for μ_r', the equality, $\mu_r' = \mu_r$, is solved to give a new value of v_r. Next, the equality, $\mu_s' = \mu_s$, is met by finding a new value for v_r'. These new values are taken as the assumed values and the procedure is repeated until the values of v_r' and v_r no longer change. Once this solution is known, the temperature is increased to the next value. For the phase diagram of figure 1, a total of seventy-five points are used in plotting each equilibrium (binodal) line.

Also shown in figure 1 is the spinodal curve found from the eigenvalue criterion. This curve is calculated by fixing the temperature and incrementing the composition to lower and lower values. For this calculation fifty increments each are used to cover both the composition and temperature ranges. At each increment the values of the pure second derivative with respect to composition and the determinant of E_{ij} are found. At high enough temperature and composition these quantities are positive. At lower values of temperature and composition the derivatives and determinant are negative. The largest composition at which one of these quantities passes through zero is taken as the spinodal composition for the given temperature. The spinodal curve calculated

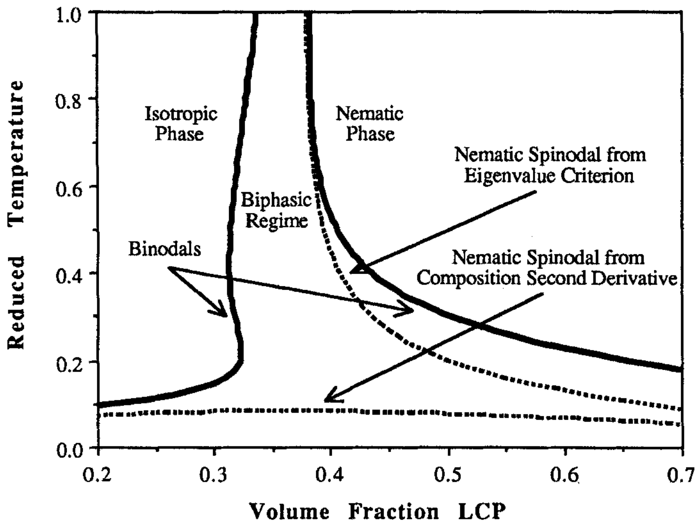

Figure 1. A temperature–composition phase diagram for a liquid-crystalline polymer (LCP) in solution. The solid curves represent the equilibrium between the biphasic region and the isotropic and nematic phases. The dashed curve represents the limit of stability for the nematic phase. The aspect ratio of the polymer is fifty ($x_r = 50$) and the relative size of the solvent is unity ($x_s = 1$). A value of zero is used for the isotropic interaction parameter ($\chi = 0$) thus the isotropic spinodal is not shown.

from the usual criterion for an incompressible binary mixture is also shown. This curve is calculated by fixing composition and incrementing the temperature to lower values; the temperature at which the second derivative passes through zero is taken as the spinodal temperature for the given composition. The same temperature and composition increments are used in the determinant case.

4. Discussion

The results of the equilibrium calculation are shown in figure 1, which is a temperature–composition phase diagram. The solid lines represent the equilibrium boundaries between the isotropic phase, the biphasic regime and the concentrated nematic phase. The ordinate is the ratio of temperature to the temperature at which the biphasic equilibrium reaches the athermal limit, that is, the temperature where energetic effects become negligible and entropy effects are dominant. It is clear that the energetics favour the formation of an anisotropic phase; they widen the biphasic regime and exclude the solvent from the nematic phase as the temperature is lowered.

That the criterion presented represents a new and distinct interpretation of what is meant by spinodal is demonstrated in figure 2. The scaled values of the second derivatives of the intensive free energy along with the determinant of E_{ij} are plotted versus the volume fraction of the nematic component for a given reduced temperature. A range of unstable compositions exists at the chosen temperature, a reduced temperature of one-third. This instability is demonstrated by the fact that the determinant is negative for a range of composition. It is seen that the determinant may be negative while the second derivative with respect to composition is positive; the usual criterion for stability in a binary system is not valid! It is also worth mentioning that the second derivative with respect to the order parameter is everywhere positive. This means that this particular instability is not entirely orientational in nature, rather

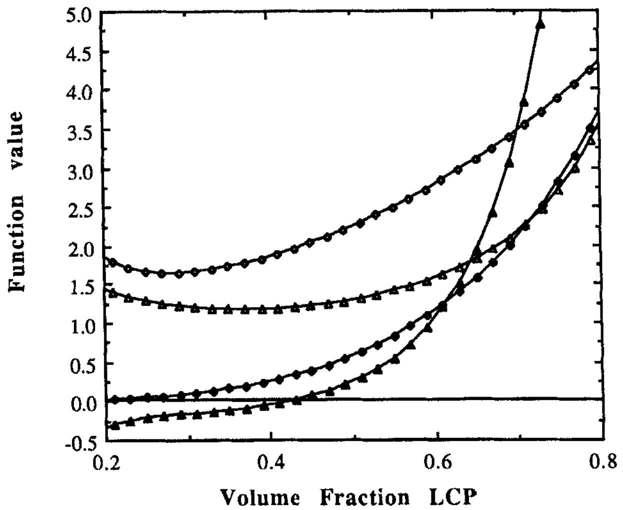

Figure 2. Values of the determinant of the stability matrix and the second derivatives of the free energy versus composition at fixed reduced temperature. Note that the determinant is negative while the second derivative with respect to composition is everywhere positive. The usual stability criterion for an incompressible binary mixture is not valid. △, (d2A/dv2); ◆, (d2A/dy2)*10e3; ▲, (Determ)*10e3; ◇, (d2A/dydv)*10e2.

it is of a mixed-mode origin. The system is unstable with respect to a variation in one of the eigenvectors. These eigenvector variations are composed of composition and order parameter fluctuations.

The nematic phase is absolutely unstable beyond the spinodal curve; it is subject to incipient phase transformation. The process of creating a new phase must occur at some finite rate; nothing, however, may be inferred about the kinetics of the process based upon these calculations. The usual criterion based solely on the second derivative with respect to composition is clearly inadequate. As the two phase region is entered the nematic phase should reach a classical stability limit. The usual criterion does not exhibit this type of behaviour; it is possible to pass from the nematic phase into the two phase region without ever crossing the spinodal.

5. Conclusions

A new, general phase stability criterion for mixtures containing nematic liquid crystals is presented. It is shown that the sign of the eigenvalues of the matrix of second derivatives of the intensive free energy dictates the stability of an equilibrium state. The conditions under which these mixtures become absolutely unstable are given. This criterion should help to clarify what is meant by spinodal decomposition when mixtures containing nematic liquid crystals or their polymeric forms are referred to in the literature. It is demonstrated that the usual criterion for phase stability in a binary system is not valid when considering a material with orientational degrees of freedom.

The processing of liquid-crystalline polymers from the nematic state is a subject of technological interest and the criterion presented here should be conceptually useful to those involved. A knowledge of the conditions under which mixtures containing liquid-crystalline polymers become unstable to infinitesimal fluctuations should be useful in understanding the post-processing morphology of these materials [3, 4, 6].

I am gratefully indebted to the Fannie and John Hertz Foundation for a Hertz Fellowship held during the course of this work. This work has benefited from a discussion with Professor D. de Fontaine of the U.C. Berkeley Materials Science Department. My thanks also to Dr Brian Devereux for a critical reading of the original manuscript.

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