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P Dayal

RA Matkar

Thein Kyu

University of Akron Main Campus, tkyu@uakron.edu

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Crystal-liquid crystal binary phase diagrams

Pratyush Dayal, Rushikesh A. Matkar, and Thein Kyu^{a)}*Department of Polymer Engineering, University of Akron, Akron, Ohio 44325-0301*

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We propose a new theoretical scheme for the binary phase diagrams of crystal-liquid crystal mixtures by a combination of a phase field model of solidification, the Flory-Huggins theory for liquid-liquid mixing and Maier-Saupe-McMillan (FH-MSM) model for nematic and smectic liquid crystal orderings. The phase field theory describes the crystal phase transition of anisotropic organic crystal and/or side chain liquid crystalline polymer crystals while the FH-MSM model explains isotropic, nematic and smectic-A phase transitions. Self-consistent calculations reveal several possible phase diagram topologies of the binary crystal-liquid crystal mixtures. The calculated phase diagrams were found to accord well to the reported experimental results. © 2006 American Institute of Physics. [DOI: 10.1063/1.2200688]

INTRODUCTION

In recent years, there has been significant interest in describing the properties of liquid crystal (LC) mixtures and polymer dispersed liquid crystals (PDLC), especially in connection with their widespread applications in electro-optical technology. On the basis of the combination of the classical Flory-Huggins (FH) theory of isotropic mixing¹ and the Maier-Saupe (MS) theory of nematic ordering,² Brochard *et al.*,³ Paiffy-Muhoray *et al.*,⁴ and Chiu and Kyu⁵ proposed theoretical descriptions for the binary phase diagrams of nematic-nematic mixtures, as well as of polymer-nematic liquid crystal mixtures. Liu and Fredrickson⁶ developed a rigorous statistical mechanical description of the free energy of liquid crystalline polymer blends involving nematic ordering. Kyu and co-workers⁷⁻¹¹ further expanded the polymer/nematic theory to the polymer/smectic A and the binary smectic-A system by incorporating the McMillan free energy of the nematic-smectic-A transition. The resulting Flory-Huggins Maier-Saupe-McMillan (FH-MSM) theory is capable of elucidating most phase diagrams of a polymer-smectic A or binary smectic-A mixture. One important phase unaccounted for thus far was the crystalline phase.

The understanding of the crystal solidification and the pattern forming aspects of the emerging crystal structures had always evolved independently of the phase transition theory of liquid crystals. Landau¹² first outlined the phenomenological model of weak crystallization within the framework of his general theory of phase transitions. The theory of weak crystallization was further refined by Kirzhnits and Nepomnyaschii¹³ and Brazovskii.¹⁴ In these models, different crystal structures, including three-dimensional lattices [body-centered cubic (BCC), face-centered cubic (FCC), and simple cubic], two-dimensional hexagonal and one-dimensional positional ordering were analyzed in terms of their relative stability. Brazovskii *et al.*¹⁵ discussed these one-dimensional and two-dimensional structures in more de-

tail and suggested that they represent smectic A and discotic liquid crystals, respectively. Furthermore, they recognized the need for the coupling between the orientational and positional degrees of freedom to properly describe a complete phase diagram of a liquid crystalline material system.

In this paper, we combine some features of the Maier-Saupe-McMillan theory of liquid crystal transitions with a phenomenological theory of crystallization based on the concept of order parameters similar in principle to one adopted by Oxtoby and Harowell.¹⁶ This generalized model will be used to describe the complete phase diagrams of binary liquid crystal mixtures, including crystalline phases. We have combined the MSM free energy for the nematic and smectic-A transition with the Flory-Huggins free energy of liquid-liquid mixing. Using the methodologies developed for earlier LC mixtures,^{9,11} the combined free energy is then minimized at each temperature and composition with respect to all order parameters. The equilibrium coexistence points are then calculated self-consistently to compare with the reported experimental phase diagrams.

The present paper is structured by first describing the details of the MSM model for a pure liquid crystal material. Second, the combined FH-MSM expression is derived for the binary LC mixtures. Subsequently, several phase diagrams have been calculated self-consistently for side-chain liquid crystalline polymer (SCLCP) and low molecular weight liquid crystal mixtures. Third, the phenomenon of crystal solidification is treated in the context of the phase field model and then compared with the experimental phase diagrams. Finally, we discuss our findings and prospects for the future development of the model.

MAIER-SAUPE-McMILLAN THEORY OF NEAT LIQUID CRYSTALS

Consider a liquid crystalline system consisting of uniaxial nonchiral molecules. The orientation and position of a molecule can be described by its director, \vec{n} and the position of its center of mass, \vec{r} . To characterize the state of a system, one can introduce a single-particle orientation distri-

^{a)}Author to whom correspondence should be addressed. Electronic mail: tkyu@uakron.edu

bution function, $f(\vec{n})$ and a single-particle density, $\rho(\vec{r})$. For uniaxial systems, the orientational ordering is defined by an order parameter,

$$S = \frac{1}{2} \int f(\vec{n}) (3 \cos^2(\vec{n}, \vec{z}) - 1) d^3\vec{n}, \quad (1)$$

where \vec{z} is the unit vector in the “preferred” direction.

In the smectic-*A* phase, the mass density is modulated along the \vec{z} direction, i.e., the average director of a molecule is perpendicular to the smectic layers. If the smectic period equals D_z , one can introduce a new order parameter m to signify the strength of smectic ordering potential,

$$m = \int \rho(0, 0, z) \cos\left(\frac{2\pi z}{D_z}\right) dz, \quad (2)$$

assuming that mass density $\rho(\vec{r}_\perp, z)$ has a peak at $z=0$. For a weak smectic ordering, the density can be approximated by a planar wave,

$$\rho(z) = \rho_0 + \delta\rho \operatorname{Re}(e^{iqz}), \quad (3)$$

where ρ_0 is the average density, and $\delta\rho$ is the amplitude of the smectic wave. In this case, $m \cong \delta\rho/\rho_0$.

We shall now construct the free energy density encompassing, at least qualitatively, nematic and smectic-*A* phase transitions among others. This free energy must include, the Maier-Saupe free energy for the nematic-isotropic (NI) transition and the McMillan free energy for the nematic-smectic-*A* (NA) transition. The most general expression for the mean-field free energy density of the Maier-Saupe-McMillan free energy may be written as

$$\frac{\beta F}{N} = -[\Sigma(S) + \Sigma(m)] - \frac{\beta\rho}{2} \times [NS^2 + Mm^2 + \Xi m^2 S + Xm^2 S^2 + \dots], \quad (4)$$

where $\beta = 1/k_B T$, the first two terms $[\Sigma(S)$ and $\Sigma(m)]$ represent entropy losses due to the orientational and positional ordering, respectively, and the terms in square brackets describe potential energy gains due to phase ordering (see Appendix A). The higher-order coupling between the order parameters, denoted by the dots, has been ignored. To further simplify our calculations, we convert the free energy of Eq. (1) to the Landau formalism by expanding the entropy terms up to the fourth order in their respective order parameters,

$$-\Sigma(S) = \frac{1}{2}aS^2 - \frac{1}{3}bS^3 + \frac{1}{4}dS^4, \quad (5)$$

$$-\Sigma(m) = \frac{1}{2}xm^2 - \frac{1}{3}vm^3 + \frac{1}{4}um^4, \quad (6)$$

where the parameters a , b , d , x , v , and u , are the coefficients for the pure material. All these entropy coefficients are calculated with the typical values of a liquid crystal: $a=6.75$, $b=13.0$, $d=17.0$, $x=2.0$, $v=0.0$, and $u=1.0$ in the context of a simple mean-field approximation in conjunction with Boltzmann-type trial functions for the single-particle distribution functions as described in the Appendix A. The enthalpy relations for the nematic and smectic transitions are identical to that determined in the Maier-Saupe-McMillan model. Thus the total free energy is as follows:

$$\frac{\beta F^{\text{MSM}}}{N} = \frac{1}{2}(a - \beta\nu)S^2 - \frac{1}{3}bS^3 + \frac{1}{4}dS^4 + \frac{1}{2}xm^2 - \frac{1}{2}vm^3 + \frac{1}{4}um^4 - \frac{1}{2}\beta C m^2 S, \quad (7)$$

where $\nu = \rho N$ and $C = \rho \Xi$. The parameters ν and C are related to the transition temperatures as follows:

$$\nu = 4.541 T_{\text{NI}},$$

$$C \cdot S(T_{\text{NA}}) = x T_{\text{NA}}. \quad (8)$$

PHASE FIELD THEORY OF CRYSTALLIZATION OF NEAT CRYSTALS

Regarding the free energy of crystal solidification, the individual calculations of entropy and enthalpy are complex and tedious, as the symmetry of a given crystal geometry of the material must be specific or known. To avoid invoking the crystal symmetry, we employ the phase field model of Oxtoby and Harowell¹⁶ and Kyu and co-workers^{17–19} for the calculation of the free energy expression of crystal solidification in polymers and small molecule systems, i.e.,

$$\frac{\beta F^{\text{PF}}}{N} = W \left[\frac{1}{2}e\psi^2 - \frac{1}{3}f\psi^3 + \frac{1}{4}g\psi^4 \right], \quad (9)$$

where e , f , and g are the coefficients of the Landau expansion of the free energy in terms of a crystal order parameter ψ ; both e and f are considered to be temperature dependent, viz., $e(T) = \zeta(T)\zeta_0(T_m)$, $f(T) = \zeta(T) + \zeta_0(T_m)$, and $g=1$. In the case of polymer crystallization, ψ may be defined as the linear crystallinity as $\psi = l/l_{\text{ext}}$, where l and l_{ext} are the thickness and equilibrium thickness of the crystal, respectively.^{17–19} In order for the Landau free energy to be applicable to a first order phase transition such as crystal solidification, it is necessary that the coefficient of the third power term must be finite, i.e., $f \neq 0$.²⁰ This free energy is characterized by an asymmetric double well that involves latent heat. However, when the coefficient of the third power term is exactly zero, such free energy, having a symmetric double well, is applicable to a second order phase transition or the first order transition only at the node. For small molecule systems, $\zeta_0=1$, whereas for polycrystalline materials it is a function of the melting temperature of the polymer crystal. In the present study, we consider only the small anisotropic molecules, hence, the phase order parameter at the solidification potential is taken as unity, i.e., $\zeta_0=1$. The coefficients ζ and W are calculated using the experimentally assessable materials parameters such as surface free energy and latent heat of crystal transition.^{18,19} Since the model does not take into consideration the columnar phase, it is reasonable to discard the coupling between ψ and S . Also, in the absence of a plastic solid phase, $M=0$.

Combining Eqs. (7) and (9), we obtain the Landau formalism of the generalized free energy density for a single component system without the columnar phase as

$$\begin{aligned} \frac{\beta F^{\text{MSMPF}}}{N} = & \frac{1}{2}(a - \beta v)S^2 - \frac{1}{3}bS^3 + \frac{1}{4}dS^4 + \frac{1}{2}xm^2 \\ & - \frac{1}{3}vm^3 + \frac{1}{4}um^4 - \frac{1}{2}\beta C m^2 S \\ & + W \left[\frac{1}{2}e\psi^2 - \frac{1}{3}f\psi^3 + \frac{1}{4}g\psi^4 \right]. \end{aligned} \quad (10)$$

Since the phase field model parameters, ζ and W , can be obtained from the known physical parameters of the materials, the final free energy expression has virtually little or no additional adjustable parameters in addition to the original Maier-Saupe-McMillan theory, yet it could describe additional phase diagram topologies including crystalline transitions. It is worth noting that the cubic terms of the Landau expression (v and f) play an important role in determining the order of the smectic A and crystal phase transitions. In our calculation, $v=0$ while $f \neq 0$. In the McMillan model of the NA transition, $v=0$, thus assuring the second-order nature of this transition, in agreement with the literature findings.²¹ Halperin *et al.*²² showed that the fluctuations of the nematic order parameter could lead, by virtue of the appearance of a small nonzero v , to the weakly first order nature of the transition. It should be emphasized that the parameter f in the Landau expression for crystal solidification must be nonzero to ensure that the crystal melting occurs via the first order. In the next section, we shall extend Eq. (10) to describe for a binary mixture, and subsequently analyze some experimentally observed topologies of phase diagrams.

FREE ENERGY DESCRIPTION FOR CRYSTAL-CRYSTAL BINARY MIXTURES

The total free energy density for binary mixtures consists of the Flory-Huggins theory for isotropic mixing, the Maier-Saupe-McMillan theory for mesophase ordering, and the phase field theory for crystal solidification, $\beta G = \beta F^{\text{FH}} + \beta F^{\text{MSM}} + \beta F^{\text{PF}}$. For an arbitrary polymer blend, the Flory-Huggins free energy density is written as

$$\frac{\beta F^{\text{FH}}}{N} = (\phi_1/r_1)\ln \phi_1 + (\phi_2/r_2)\ln \phi_2 + \chi_{12}\phi_1\phi_2, \quad (11)$$

where r_1 and r_2 are the number of sites occupied by molecules 1 and 2, respectively (usually, $r_i=1$ for a low-molecular-weight compound, and is larger than unity for a polymer); in the present case both r_i values are taken as unity. ϕ_1 and ϕ_2 are volume fractions of components 1 and 2 (related by the incompressibility constraint $\phi_1 + \phi_2 = 1$). The parameter χ_{12} (the Flory-Huggins interaction parameter) is usually written in the form $\chi_{12} = A + B/T$, where A and B are constants. B is proportional to the interchange energy related to the heats of vaporization of the constituents and χ_{12} is inversely proportional to absolute temperature. If $\chi_{12} > \chi_{\text{crit}} = 0.5(r_1^{-1/2} + r_2^{-1/2})^2$, the liquid-liquid phase separation takes place.

The free energy density of liquid crystal ordering can be derived from Eq. (4) by separating the interaction terms and the entropic terms for the Maier-Saupe-McMillan model and introducing the cross-interaction contributions.

$$\begin{aligned} g^{\text{MSM}} = & (F^{\text{MSM}}/Nk_B T) \\ = & \left[\frac{1}{2}a_1S_1^2 - \frac{1}{3}b_1S_1^3 + \frac{1}{4}d_1S_1^4 + \frac{1}{2}x_1m_1^2 + \frac{1}{3}v_1m_1^3 + \frac{1}{4}u_1m_1^4 \right] \phi_1 + \left[\frac{1}{2}a_2S_2^2 - \frac{1}{3}b_2S_2^3 + \frac{1}{4}d_2S_2^4 + \frac{1}{2}x_2m_2^2 + \frac{1}{3}v_2m_2^3 + \frac{1}{4}u_2m_2^4 \right] \phi_2 \\ & - \frac{\beta}{2}(\nu_{11}S_1^2\phi_1^2 + 2\nu_{12}S_1S_2\phi_1\phi_2 + \nu_{22}S_2^2\phi_2^2) - \frac{\beta}{2}(C_{11}m_1^2S_1 + 2C_{12}m_1m_2\sqrt{S_1S_2} + C_{22}m_2^2S_2), \end{aligned} \quad (12)$$

where the first two terms represent pure entropic contributions (entropy losses from orientational and transverse ordering for each component), and the next two terms correspond to the enthalpic contributions (in units of $\beta=1/k_B T$). These terms represent the nematic ordering, and the McMillan coupling between the orientational and positional degrees of freedom (smectic A). The cross terms in the interaction potentials for a given mixture may be evaluated in terms of the geometric means from the parameters ν_{11} , C_{11} , ν_{22} , C_{22} that are specific to pure components 1 and 2, i.e.,

$$\begin{aligned} \nu_{12} = & c_\nu \sqrt{\nu_{11}\nu_{22}}, \\ C_{12} = & c_c \sqrt{C_{11}C_{22}}. \end{aligned} \quad (13)$$

In practice, most liquid crystals can crystallize upon lowering the temperature. To determine the free energy of mixing of the crystalline species, we propose the existence of

interaction terms that lead to crystal-liquid and crystal-crystal demixings. In view of the phenomenological arguments, the interaction terms for crystal-liquid segregation are analogous to the χ_{12} liquid-liquid interaction parameter of the Flory approach.²³ These interaction parameters are deducted to be proportional to the enthalpies of crystallization such that the intracrystalline chain interaction terms can be expressed as, $\omega_{11} \sim \Delta H_1^c/RT$ and $\omega_{22} \sim \Delta H_2^c/RT$, where ΔH_1^c and ΔH_2^c are enthalpies of crystallization of components 1 and 2, respectively. It should be noted here that intracrystalline chain interaction terms ω_{11} and ω_{22} are proportional to $(\Delta H_1^c + \Delta H_1^m)/RT$ and $(\Delta H_2^c + \Delta H_2^m)/RT$, respectively, where ΔH_i^m is the heat of mixing for crystal and amorphous parts. Since the heat of mixing ΔH_i^m is negligibly small as compared to heat of crystallization, hence we get the aforementioned expressions for ω_{11} and ω_{22} . $\omega_{12} = c_\omega \sqrt{\omega_{11}\omega_{22}}$ is the cross-interaction term to describe the crystal-crystal segregation, where c_ω is equivalent to the c_ν and c_c parameter de-

fined for the case of nematic and smectic mixtures. It is expressed as the geometric mean of the intracrystal chain interaction terms^{9,11} for consistency. $c_\omega=1$ denotes the ideal solid solution where the crystal of each component is completely miscible in the other. However, when $c_\omega = \omega_{12}/\sqrt{\omega_{11}\omega_{22}} > 1$, the dissimilar chains prefer to crystallize in the mixed crystalline state (hereafter called co-crystals)

and vice versa when, $c_\omega = \omega_{12}/\sqrt{\omega_{11}\omega_{22}} < 1$, the individual chains prefer to crystallize in the pure constituents, thereby forming separate individual crystals. These neat individual crystals tend to reject the amorphous materials from their crystallizing fronts. Thus, the generalized equation for describing the nematic-smectic-A-crystal transitions may be expressed in what follows:

$$g^{\text{MSMPF}} = (F^{\text{MSMPF}}/Nk_B T) \\ = \left[\frac{1}{2}a_1 S_1^2 - \frac{1}{3}b_1 S_1^3 + \frac{1}{4}d_1 S_1^4 + \frac{1}{2}x_1 m_1^2 + \frac{1}{3}v_1 m_1^3 + \frac{1}{4}u_1 m_1^4 \right] \phi_1 + \left[\frac{1}{2}a_2 S_2^2 - \frac{1}{3}b_2 S_2^3 + \frac{1}{4}d_2 S_2^4 + \frac{1}{2}x_2 m_2^2 + \frac{1}{3}v_2 m_2^3 + \frac{1}{4}u_2 m_2^4 \right] \phi_2 \\ - \frac{\beta}{2}(\nu_{11} S_1^2 \phi_1^2 + 2\nu_{12} S_1 S_2 \phi_1 \phi_2 + \nu_{22} S_2^2 \phi_2^2) - \frac{\beta}{2}(C_{11} m_1^2 S_1 + 2C_{12} m_1 m_2 \sqrt{S_1 S_2} + C_{22} m_2^2 S_2) \\ + W_1 \left[\frac{1}{2}e_1 \psi_1^2 - \frac{1}{3}f_1 \psi_1^3 + \frac{1}{4}g_1 \psi_1^4 \right] \phi_1 + W_2 \left[\frac{1}{2}e_2 \psi_2^2 - \frac{1}{3}f_2 \psi_2^3 + \frac{1}{4}g_2 \psi_2^4 \right] \phi_2 - \frac{\beta}{2} \phi_1 \phi_2 (\omega_{11} \psi_1^2 + 2\omega_{12} \psi_1 \psi_2 + \omega_{22} \psi_2^2). \quad (14)$$

As demonstrated in Appendix B, the last term in Eq. (14) can be expressed in an analogous form of the smectic or nematic interactions shown in the fourth and fifth terms of Eq. (14), except that the second coefficient of the phase field potential gets modified slightly without sacrificing any physical significance [see Eq. (B4)]. To evaluate the free energy given by Eq. (14), each order parameter needs to be evaluated in the mixture as a function of composition and temperature. This can be achieved by minimizing the free energy with respect to the order parameters: S_j , m_j , and ψ_j , i.e.,

$$\frac{\partial g^{\text{MSMPS}}}{\partial S_j} = 0, \quad \frac{\partial g^{\text{MSMPF}}}{\partial m_j} = 0, \quad \text{and} \quad \frac{\partial g^{\text{MSMPF}}}{\partial \psi_j} = 0. \quad (15)$$

This approach yields six simultaneous equations which are solved by an iterative procedure to determine the values of order parameters as a function of composition and temperature. Once the order parameters at the phase transition points have been determined, the free energy can be calculated subsequently by equating the chemical potentials in the two phases in conjunction with the double-tangent approach.

Figure 1 depicts the phase diagram of a hypothetical mixture showing nematic, smectic, and crystal phase transitions. The physical and material parameters utilized for construction of this phase diagram are $r_1 = 1$, $r_2 = 1$, $A = 0$, $B = 730$ K, $(\nu_{11}/4.54k_B) = 385$ K, $(\nu_{22}/4.54k_B) = 375$ K, $(C_{11}/k_B) = 1128$ K, $(C_{22}/k_B) = 1096$ K, $\Delta H_1 = 12.5$ kJ/mol, $\Delta H_2 = 12.5$ kJ/mol, $c_\nu = 0.8$, $c_c = 0.9$, $c_\omega = 0.85$, $T_{Cr1} = 325$ K, and $T_{Cr2} = 315$ K. The condition, $B = 730$ K, makes the FH interaction parameter to be $\chi_{12} > \chi_{\text{crit}}$, and thus the upper critical solution temperature (UCST) envelope protrudes above the coexistence boundaries all mesophase transitions manifested by Eq. (14). At much lower temperatures, the two crystalline phases (Cr–Cr) coexist. At an elevated temperature, the coexistence of nematic-liquid (N–L) occurs at the compositions rich in either phase, while the liquid-liquid (L–L) coexistence region develops at the intermediate compositions. At intermediate temperatures one can discern the Cr–SmA, SmA–SmA,

N–SmA, N–N, and L–N coexistence regions in ascending order. At extreme compositions, the neat nematic, neat smectic, and neat crystal regions corresponding to the pure components are identifiable. Recall that the cross-interaction terms, c_ν , c_c , and c_ω , are the measures of relative strength of interaction between dissimilar mesogens to that of the same mesogens. When these values increase the corresponding phases are more stable in the pure state as compared to the mixed state, and thereby the coexistence gaps become narrower.

Figure 2 exhibits the binary phase diagram with the strength of cross-interaction terms being raised to $c_\nu = 0.96$, $c_c = 0.96$, and $c_\omega = 0.92$ from those in Fig. 1 with a critical temperature of $B = 430$ K, i.e., $\chi_{12} \ll \chi_{\text{crit}}$. It should be pointed out that some gaps can be noticed in the coexistence curves

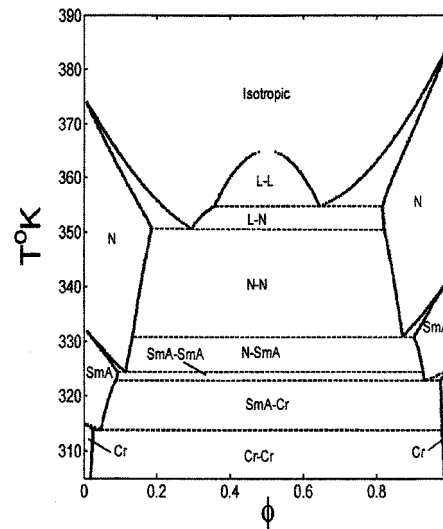


FIG. 1. Phase diagram of a hypothetical mixture showing various coexistence regions indicated by corresponding symbols, intersecting with various phase transition lines. The calculation was undertaken using the following parameters: $r_1 = 1$, $r_2 = 1$, $A = 0$, $B = 730$ K, $(\nu_{11}/4.54k_B) = 385$ K, $(\nu_{22}/4.54k_B) = 375$ K, $(C_{11}/k_B) = 1128$ K, $(C_{22}/k_B) = 1096$ K, $\Delta H_1 = 12.5$ kJ/mol, $\Delta H_2 = 12.5$ kJ/mol, $c_\nu = 0.8$, $c_c = 0.9$, $c_\omega = 0.85$, $T_{Cr1} = 325$ K, and $T_{Cr2} = 315$ K.

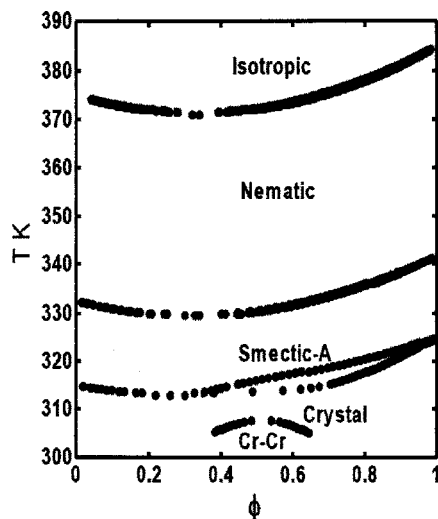


FIG. 2. Phase diagram of a hypothetical mixture showing the isotropic, nematic, smectic A, and solid crystal coexistence regions. The calculation was undertaken with the parameters of Fig. 1, except $c_v=0.96$, $c_c=0.96$, and $c_\omega=0.92$.

which are the consequence of the very narrow coexistence region in which the free energy minima are no longer well resolved. Even after increasing the grid resolution for two orders of magnitude, there remain some gaps, but smaller, in the phase diagrams (Fig. 2). Despite the existence of such gaps in the plot, the trend can still be captured. In the descending order of temperature, one can identify the isotropic+nematic, pure nematics, nematic+smectic, pure smectics, and smectic+crystal coexistence regions. The coexistence of the crystal-crystal phases occurs at a much lower temperature as depicted in Fig. 2. If these cross-interaction terms were raised to an ideal situation, i.e., $c_v=1.0$, $c_c=1.0$, and $c_\omega=1.0$, all the liquids and solidus lines virtually coincide on each other and vary linearly with composition, which is representative of the ideal mixture (figure not shown, because the same trends of nematics and smectics have been reported elsewhere⁷).

In Fig. 3 is shown the phase diagram when the strength of cross interaction were further increased to $c_v=1.10$, $c_c=1.10$, and $c_\omega=1.10$. Since all these cross-interaction terms are larger than unity, the nematic, smectic, and crystal phases are favored to form between dissimilar mesogens relative to those of the neat mesogens. That is to say the mesophase structures are more stable in the mixed state than those of their neat phases, as demonstrated by the enhanced transition temperatures at the intermediate compositions. Except for the crystal azeotrope, the enhanced transition temperatures have been experimentally verified for the nematics⁷ and smectics.¹⁰ It should also be noted that although the value of parameter $B=730$ K is the same as that in the first case, the liquid-liquid coexistence has now vanished.

In order to illustrate the predictive capabilities of the present generalized theory, we have calculated phase diagrams for some specific liquid crystal mixtures. First, we performed an experiment on a mixture of smectic liquid crystal, viz., cyanobiphenyl derivative (12CB) (commercially known as K36) and side-on SCLCP [i.e., poly-

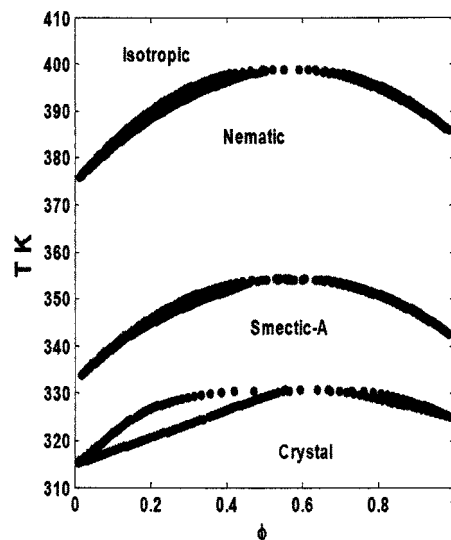


FIG. 3. Azeotrope phase diagram of a hypothetical mixture showing the isotropic, nematic, smectic A, solid crystal, and crystal-crystal coexistence regions. The calculation was undertaken with the parameters of Fig. 1, except $c_v=1.10$, $c_c=1.10$, and $c_\omega=1.10$.

methacrylate backbone grafted with 2,5 bis-(4-butoxy benzyloxy) benzoate mesogen connected by a butyl group, hereafter abbreviated as sSCLCP]. The liquid crystal K36 has a phase sequence of I-S_{mA}-Cr, whereas the sSCLCP polymer exhibits only the I-N transition in the temperature range investigated. In our experiments, a distinct smectic-A-crystal transition was observed in the differential scanning calorimetry (DSC) studies for several compositions as shown by the symbols in the phase diagram (Fig. 4). In a second experiment, we utilized a binary mixture of octylcyanobiphenyl (8CB) and octyloxycyanobiphenyl (8OCB) which are 4-cyano-4-alkylbiphenyls (*n*CB) and 4-cyano-4'-alkoxybiphenyls (*n*OCB), respectively, where *n* denotes

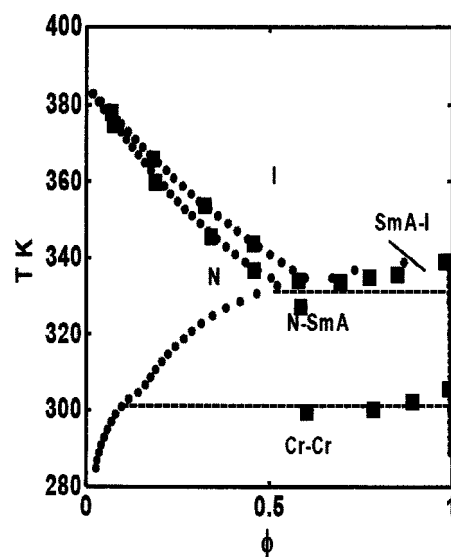


FIG. 4. Comparison between the calculated and experimental phase diagram of a K36/sSCLCP calculated using the following values: $r_1=1$, $r_2=2.25$, $A=0$, $B=129$ K, $(v_{11}/4.54k_B)=327$ K, $(v_{22}/4.54k_B)=385$ K, $(C_{11}/k_B)=1360$ K, $(C_{22}/k_B)=0$ K, $\Delta H_1=29.3$ kJ/mol, $\Delta H_2=13.2$ kJ/mol, $c_v=0.9$, $c_c=1.0$, $c_\omega=1.0$, $T_{Cr1}=306$ K, and $T_{Cr2}=94$ K. The symbols indicate the phase transition points by DSC experiments scanned at 10 °C/min.

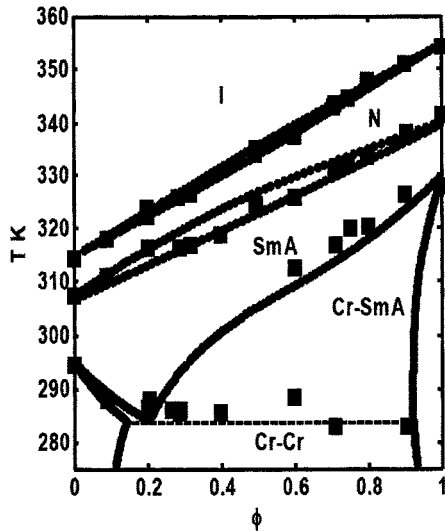


FIG. 5. Comparison between the calculated and experimental phase diagram of a 8CB/8OCB calculated using the following values: $r_1=1$, $r_2=1$, $A=0$, $B=141.4$ K, $(\nu_{11}/4.54k_B)=355$ K, $(\nu_{22}/4.54k_B)=315$ K, $(C_{11}/k_B)=1214$ K, $(C_{22}/k_B)=1118$ K, $\Delta H_1=9.6$ kJ/mol, $\Delta H_2=3.8$ kJ/mol, $c_v=1.0$, $c_c=1.0$, $c_\omega=0.5$, $T_{Cr1}=330$ K, and $T_{Cr2}=295$ K. The symbols indicate the phase transition points by DSC experiments scanned at $10^\circ\text{C}/\text{min}$.

the number of carbon atoms in the alkyl group.²⁴ The sequence of phase transitions for 8CB and 8OCB is Cr-S_{mA}-N-I in both cases. The experimental phase diagram of this system was reported to obtain by DSC.²⁴

To calculate the phase diagram, we conducted numerical minimization of the free energy of Eq. (14) for a broad range of temperatures by varying the volume fractions of components between 0 and 1 with a grid step of 0.001. For each temperature-composition point, free energy was calculated for each of the four phases (isotropic, nematic, smectic A, and crystal); within each phase (except isotropic), we used the iterative procedure, which provides a better convergence than the conventional steepest decent method in minimizing the free energy with respect to all relevant order parameters. A common tangent algorithm was utilized to determine the coexistence regions between different phases.

In Fig. 4, the calculated phase diagram for the K36-sSCLCP system is shown together with some experimental points (filled diamonds).¹⁰ The experimental material parameters and conditions utilized are $r_1=1$, $r_2=2.25$, $A=0$, $B=129$ K, $(\nu_{11}/4.54k_B)=327$ K, $(\nu_{22}/4.54k_B)=385$ K, $(C_{11}/k_B)=1360$ K, $(C_{22}/k_B)=0$ K, $\Delta H_1=29.3$ kJ/mol, $\Delta H_2=13.2$ kJ/mol, $c_v=0.9$, $c_c=1.0$, $c_\omega=1.0$, $T_{Cr1}=306$ K, and $T_{Cr2}=94$ K. It is apparent that the present generalized free energy is capable of describing the phase diagram of the K36-sSCLCP system reasonably well. At low temperatures, increasing the concentration of K36 leads to the N-Cr transition, showing a broad coexistence region. Above 305 K, the LC (K36) is in the smectic phase, but it coexists with nematic phase of sSCLCP, exhibiting a broad two-phase region. At $T=330$ K, there is a triple point I+N+S_{mA}. Between 330 and 340 K, one observes the coexistence of N-I-S_{mA} phases. Above 340 K, only the nematic-isotropic transition is discernible.

Figure 5 exhibits the calculated phase diagram of 8CB/

8OCB system utilizing the following experimental and material parameters: $r_1=1$, $r_2=1$, $A=0$, $B=141.4$ K, $(\nu_{11}/4.54k_B)=355$ K, $(\nu_{22}/4.54k_B)=315$ K, $(C_{11}/k_B)=1214$ K, $(C_{22}/k_B)=1118$ K, $\Delta H_1=9.6$ kJ/mol, $\Delta H_2=3.8$ kJ/mol, $c_v=1.0$, $c_c=1.0$, $c_\omega=0.5$, $T_{Cr1}=330$ K, and $T_{Cr2}=295$ K. It is evident that the theoretical predictions are in good accord with the experimental coexistence lines. Below, the triple point at $T=284$ K, the crystal phase of 8CB is in equilibrium with crystal phase of 8OCB. As the temperature is increased, Cr-S_{mA}, S_{mA}-N, and N-I transitions are observed in sequel.

CONCLUSIONS

We have developed a generalized theory consisting of FH free energy of mixing, MSM free energy of LC phase transition and the Landau-type free energy (also known as the phase field model) of solidification. We have demonstrated that this new model is capable of describing the phase behavior of binary liquid crystal and crystal mixtures, covering a crystalline phase together with the liquid crystalline (nematic and smectic) and isotropic phases. The present model has been tested satisfactorily to conform to the experimental phase diagram of the liquid crystal-sSCLCP system (K36/sSCLCP), as well as those of the liquid crystal mixtures (8CB/8OCB). It is concluded that the present model can describe most topologies of binary crystal/liquid crystal equilibrium phase diagrams, except for re-entrant, columnar, and tilted smectics.

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APPENDIX A: CALCULATION OF ENTROPIC TERMS FOR THE PURE COMPONENTS

In order to determine the coefficients of the Landau expansion of the orientational and one-dimensional (smectic) positional entropies, we first write down their “ideal-gas” mean-field expressions in terms of single-particle distribution functions,

$$\Sigma(S) = - \int f(n) \ln[4\pi f(n)] d^3n, \quad (\text{A1})$$

$$\Sigma(m) = - \int \rho(z) \ln[\rho(z)/\rho_0] dz. \quad (\text{A2})$$

The single-particle distribution functions are parameterized as follows:

$$f(n) = A \exp[L(3 \cos^2(n, z) - 1)/2], \quad (\text{A3})$$

$$\rho(z) = \rho_0 B \exp[M \cos(2\pi z/D_z)], \quad (\text{A4})$$

where A and B are normalization constants, while L and M determine the strengths of orientational and positional ordering, respectively.

To approximate Eq. (A1) with a fourth-degree polynomial in S , we compute $\Sigma(S)$ and S for a set of one hundred values of L uniformly distributed between 0 and 15 (corresponding to the values of S between 0 and 0.95). Then, the obtained function $\Sigma(S)$ is approximated by a polynomial (2) whose coefficients are determined by the least-squares approach. The resulting values are $a=6.75$, $b=13.0$, and $d=17.0$; the subscripts 1 and 2 are not necessary because these parameters are meant for the pure components. Minimizing the Maier-Saupe free energy with these coefficients yields the following relationship between the transition temperature T and the potential strength ν :

$$\nu = 4.54T_{\text{NI}}, \quad (\text{A5})$$

which agrees very well with the exact Maier-Saupe relationship $\nu=4.54T$. In fact, the agreement is much better than if we would simply expand the (implicit) function $\Sigma(S)$ in a Taylor series near $S=0$ up to the fourth order, since in the nematic phase, S is usually in the range of 0.5–0.8.

It is possible to use a similar technique in describing the smectic entropy Eq. (A2). However, for the smectic phase, the ordering is usually small, and it is more important to correctly capture the limit of small m . Thus, one can expand Eq. (A4) in powers of M by substituting this expansion into Eq. (A2), and calculating the entropy as a function of M . After some tedious algebra, we get

$$-\Sigma(m) = \frac{M^2}{4} - \frac{3M^4}{64}. \quad (\text{A6})$$

The relationship between M and m is given by

$$M = 2m \left(1 + \frac{m^2}{4} \right), \quad (\text{A7})$$

so the final result is (in the limit of small m):

$$-\Sigma(m) = m^2 + \frac{m^4}{4}. \quad (\text{A8})$$

Thus, $x=2.0$, $\nu=0$, and $u=1.0$.

APPENDIX B: ANALOGY BETWEEN FREE ENERGY DESCRIPTIONS OF SOLIDIFICATION OF BINARY CRYSTAL/CRYSTAL BLENDS AND OF CRYSTAL/LIQUID CRYSTAL BLENDS

The free energy for a two-crystalline system may be expressed in the context of a phase field theory of crystal solidification as follows:

$$g^{\text{PF}} = W_1 \left[\frac{1}{2} e_1 \psi_1^2 - \frac{1}{3} f_1 \psi_1^3 + \frac{1}{4} g_1 \psi_1^4 \right] \phi_1 + W_2 \left[\frac{1}{2} e_2 \psi_2^2 - \frac{1}{3} f_2 \psi_2^3 + \frac{1}{4} g_2 \psi_2^4 \right] \phi_2 + \frac{\beta}{2} \phi_1 \phi_2 (\omega_{11} \psi_1^2 - 2\omega_{12} \psi_1 \psi_2 + \omega_2^2). \quad (\text{B1})$$

By virtue of the incompressibility conditions, $\phi_1 + \phi_2 = 1$, Eq. (B1) can be rewritten as

$$g^{\text{PF}} = W_1 \left[\frac{1}{2} e_1 \psi_1^2 - \frac{1}{3} f_1 \psi_1^3 + \frac{1}{4} g_1 \psi_1^4 \right] \phi_1 + W_2 \left[\frac{1}{2} e_2 \psi_2^2 - \frac{1}{3} f_2 \psi_2^3 + \frac{1}{4} g_2 \psi_2^4 \right] \phi_2 + \frac{\beta}{2} [\omega_{11} \psi_1^2 \phi_1 (1 - \phi_1) - 2\omega_{12} \psi_1 \psi_2 \phi_1 \phi_2 + \omega_{22} \psi_2^2 \phi_2 (1 - \phi_2)] \quad (\text{B2})$$

or,

$$g^{\text{PF}} = W_1 \left[\frac{1}{2} e_1 \psi_1^2 - \frac{1}{3} f_1 \psi_1^3 + \frac{1}{4} g_1 \psi_1^4 \right] \phi_1 + W_2 \left[\frac{1}{2} e_2 \psi_2^2 - \frac{1}{3} f_2 \psi_2^3 + \frac{1}{4} g_2 \psi_2^4 \right] \phi_2 - \frac{\beta}{2} [\omega_{11} \psi_1^2 \phi_1^2 + 2\omega_{12} \psi_1 \psi_2 \phi_1 \phi_2 + \omega_{22} \psi_2^2 \phi_2^2] + \frac{\beta}{2} \omega_{11} \psi_1^2 \phi_1 + \frac{\beta}{2} \omega_{22} \psi_2^2 \phi_2. \quad (\text{B3})$$

Rearranging the terms leads to

$$g^{\text{PF}} = W_1 \left[\frac{1}{2} \left(e_1 + \frac{\beta \omega_{11}}{W_1} \right) \psi_1^2 - \frac{1}{3} f_1 \psi_1^3 + \frac{1}{4} g_1 \psi_1^4 \right] \phi_1 + W_2 \left[\frac{1}{2} \left(e_2 + \frac{\beta \omega_{22}}{W_2} \right) \psi_2^2 - \frac{1}{3} f_2 \psi_2^3 + \frac{1}{4} g_2 \psi_2^4 \right] \phi_2 - \frac{\beta}{2} [\omega_{11} \psi_1^2 \phi_1^2 + 2\omega_{12} \psi_1 \psi_2 \phi_1 \phi_2 + \omega_{22} \psi_2^2 \phi_2^2]. \quad (\text{B4})$$

Equation (B4) is the free energy of the crystal/liquid crystal blend written in the analogous form of the free energy description for the crystal/crystal blend [Eq. (B1)], except that the coefficient of the second order term in the Landau expansion gets modified as exemplified in Eq. (B4).

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