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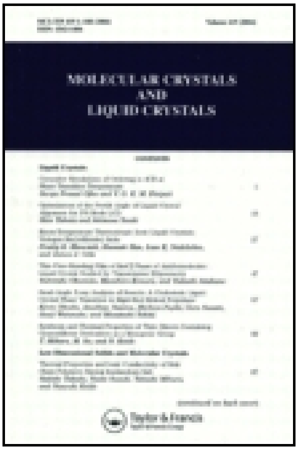

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Mean Field Theory of Binary Mixtures of Nematic Liquid Crystals

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Mean Field Theory of Binary Mixtures of Nematic Liquid Crystals

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Molecular field theory is used to determine the temperature-composition phase diagram and component order parameters of binary mixtures of nematic liquid crystals. A rotationally invariant form of the Maier-Saupe pseudopotential is generalised to two-component mixtures; the parameters of the theory are the ratios of transition temperatures, number densities and isotropic interaction strengths of the pure components. The possibility of induced biaxiality and the effects of an external field are discussed. The model predicts a rich variety of phase behaviour. For dissimilar constituents, coexisting nematic-isotropic and nematic-nematic phases are predicted in agreement with experiment and hard particle theories. In general, the order parameters of the two constituents differ in a given phase; changing the sign of the interspecies interaction term in the pseudopotential results in the appearance of a biaxial solution. This biaxial phase is shown to be unstable however, and, on quenching, is expected to exhibit spinodal decomposition.

INTRODUCTION

Binary mixtures of liquid crystals are of considerable practical and theoretical interest. Display devices utilise mixtures whose physical characteristics are more suited for device applications than those of pure materials, while the phase behaviour of liquid crystal mixtures is far richer than that of isotropic fluid mixtures.

A large variety of coexisting phases have been observed in binary mixtures; among these are coexisting nematic and isotropic phases[1–3]

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and coexisting nematic-nematic phases.[4] Recently, biaxial phases have also been observed.[5-8] Considerable work in the theory of liquid crystalline mixtures has been carried out (see for example ref. 9), ranging from general thermodynamic approaches[10] to statistical mechanical methods based on lattice models,[11-13] hard particle theories,[14-15] molecular field theories[16-20] and combinations of these.[21] A particularly useful approach has been extension of the Maier–Saupe (M-S) theory for pure nematics to binary mixtures.[19] This approach has enabled the determination of phase diagrams, component order parameters and coexistence curves and has allowed some comparison with experiment.[3,22]

In this paper, we extend this molecular field approach to include the effects of external fields and isotropic interactions and to allow for the possibility of induced biaxiality. The M-S pseudopotential, expressed in the rotationally invariant form,[23] is generalised to two component mixtures. Minimising the free energy expressed in terms of this pseudopotential enables the calculation of component order parameters and determination of the phase diagrams. A simple method is proposed for the unambiguous determination of the coexistence of two (liquid) phases. In addition to the effects of the isotropic part of the interaction and the effects of external fields, the behaviour of mixtures consists of components which favour alignment perpendicular to each other is of particular interest. Previous lattice[13] and more recent hard particle[15] and lattice/van der Waals[21] theories predict a stable biaxial phase for a mixture of rods and plates, which undergoes a second order transition to either a uniaxial nematic or an isotropic phase. The extended M-S theory presented here also locates this biaxial phase, which, however, is found to coincide with the spinodal region associated with material instability. In equilibrium, two coexisting uniaxial nematic phases are lower in free energy than the biaxial one; however, on rapid quenching the biaxial phase is accessible and is predicted to exhibit spinodal decomposition.

Theory

a. The Single Particle Pseudopotential

In the usual formulation of the Maier–Saupe (M-S) theory, a cylindrically symmetric mesogen whose symmetry axis is the direction of the unit vector $\hat{n}$ has orientational potential energy

$$\epsilon(\hat{n}) = -AQP_2(\cos\theta) \qquad (1)$$

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where θ is the angle between $\hat{n}$ and the direction of average molecular orientation called the 'director', $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$, $Q = \langle P_2(\cos\theta)\rangle$ where the brackets $\langle\ \rangle$ denote the ensemble average, and A is a constant such that AQ is the molecular field responsible for orientation due to other molecules in the fluid. Eq. (1) is not complete or strictly correct, however, since its evaluation requires an a priori knowledge of the director direction, and also because it predicts an average energy per molecule $\langle\epsilon(\hat{n})\rangle = -AQ^2$ which is too large by a factor of two.

The correct single particle pseudopotential may be obtained from the intermolecular potential $W(\mathbf{r}_{12},\hat{n}_1,\hat{n}_2)$, where $\mathbf{r}_{12}$ is the vector from the center of molecule 1 to that of 2, as follows. If the potential W is pairwise additive, then it can be shown exactly[24] that

$$\frac{\partial}{\partial n_{1_\alpha}}\epsilon(\hat{n}_1) = \rho\int\left[\frac{\partial}{\partial n_{1_\alpha}}W(\mathbf{r}_{12},\hat{n}_1,\hat{n}_2)\right]g(\mathbf{r}_{12},\hat{n}_1,\hat{n}_2)\,d^3\mathbf{r}_{12}\,f(\hat{n}_2)\,d^2\hat{n}_2 \tag{2}$$

where n_{1_α} is a component of $\hat{n}_1$, ρ is the number density, $g(\mathbf{r}_{12},\hat{n}_1,\hat{n}_2)$ is the radial distribution function, $f(\hat{n})$ is the single particle orientational distribution function, and $d^2\hat{n} = d\Omega/4\pi = \sin\theta\, d\theta\, d\phi/4\pi$. The mean field approximation consists of ignoring the dependence of the radial distribution on molecular orientation, which enables the integration of Eq. (2). This gives

$$\epsilon(\hat{n}_1) = \text{const.} + \rho\int W(\mathbf{r}_{12},\hat{n}_1,\hat{n}_2)g(\mathbf{r}_{12})\,d^3\mathbf{r}_{12}\,f(\hat{n}_2)\,d^2\hat{n}_2. \tag{3}$$

The M-S pseudopotential is obtained by truncating the expansion of the integral over $\mathbf{r}_{12}$ in Eq. (3) in Legendre polynomials after the second term; that is, by letting

$$\rho\int W(\mathbf{r}_{12},\hat{n}_1,\hat{n}_2)g(\mathbf{r}_{12})\,d^3\mathbf{r}_{12} = -\rho\gamma - \rho U P_2(\hat{n}_1\cdot\hat{n}_2).$$

It is useful to define $\sigma_{i_{\alpha\beta}} = \frac{1}{2}(3n_{i_\alpha}n_{i_\beta} - \delta_{\alpha\beta})$ (where $\delta_{\alpha\beta}$ is the Kronecker delta) and $S_{\alpha\beta} = \langle\sigma_{\alpha\beta}\rangle$; then $P_2(\hat{n}_1\cdot\hat{n}_2) = \frac{2}{3}\sigma_{1_{\alpha\beta}}\sigma_{2_{\beta\alpha}}$ where summation is implied over repeated greek indices, and Eq. (3) gives

$$\epsilon(\hat{n}) = \text{const.} - \rho\gamma - \tfrac{2}{3}\rho U S_{\alpha\beta}\sigma_{\beta\alpha}. \tag{4}$$

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The constant in Eq. (4) can be determined by considering the total potential energy of N molecules, obtained by taking the derivative of the configurational free energy F with respect to $\beta = 1/kT$. This gives

$$
\begin{aligned}
\epsilon_{\mathrm{TOT.}} &= \frac{1}{\beta}\frac{\partial}{\partial\beta}(\beta F) \\
&= \frac{N}{2}\rho\int W(\mathbf{r}_{12},\hat{n}_1,\hat{n}_2)g(\mathbf{r}_{12})d^3\mathbf{r}_{12}f(\hat{n}_1)f(\hat{n}_2)d^2\hat{n}_1\,d^2\hat{n}_2 \\
&= \frac{N}{2}\left(-\rho\gamma - \frac{2}{3}\rho U S_{\alpha\beta}S_{\beta\alpha}\right). \qquad (5)
\end{aligned}
$$

Since $\epsilon_{\mathrm{TOT.}}$ must also equal

$$N\langle\epsilon(\hat{n})\rangle = N(\mathrm{const.} - \rho\gamma - \frac{2}{3}\rho U S_{\alpha\beta}S_{\beta\alpha}),$$

the constant of integration can be determined. If a magnetic field $\mathbf{H}$ is also present, a molecule has additional orientational energy $-\frac{1}{3}\Delta\kappa H_\alpha H_\beta\sigma_{\beta\alpha}$ where $\Delta\kappa = \kappa_{\parallel} - \kappa_{\perp}$ is the anisotropy of molecular susceptibility and H_α is a component of $\mathbf{H}$. Thus, finally, the single particle pseudopotential becomes

$$\epsilon(\hat{n}) = -\tfrac{1}{2}\rho\gamma - \tfrac{2}{3}\rho U S_{\alpha\beta}\sigma_{\beta\alpha} + \tfrac{1}{3}\rho U S_{\alpha\beta}S_{\beta\alpha} - \tfrac{1}{3}\Delta\kappa H_\alpha H_\beta\sigma_{\beta\alpha}. \qquad (6)$$

As required, this pseudopotential is independent of choice of coordinate systems and does not require an a priori knowledge of the director direction for its evaluation. Equilibrium values of the elements of the order parameter tensor $S_{\alpha\beta}$ are those which minimise the free energy; this minimisation gives rise to the self-consistent equations

$$S_{\alpha\beta} = \frac{\int \sigma_{\alpha\beta}e^{-\beta\epsilon(\hat{n})}\,d^2\hat{n}}{\int e^{-\beta\epsilon(\hat{n})}\,d^2\hat{n}}. \qquad (7)$$

Eq. (7) has an infinite number of solutions, corresponding to all possible orientations of a coordinate system. Since $S_{\alpha\beta}$ is normal (and traceless), it is diagonal in a principal axis system (PAS). It is convenient to introduce the notation $\sigma_{xx} = -\frac{1}{2}(q - p)$, $\sigma_{yy} = -\frac{1}{2}(q + p)$ and $\sigma_{zz} = q$ where $q = \frac{1}{2}(3\cos^2\theta - 1)$ and $p = \frac{3}{2}\sin^2\theta\cos 2\phi$ and θ and ϕ are the usual polar and azimuthal angles defining the direction of $\hat{n}$. The uniaxial and biaxial order parameters are, respectively,

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$Q = \langle q \rangle$ and $P = \langle p \rangle$. In a PAS, the pseudopotential becomes

$$\epsilon(\hat{n}) = -\tfrac{1}{2}\rho\gamma - \tfrac{1}{3}\rho U(3Qq + Pp) + \tfrac{1}{6}\rho U(3Q^2 + P^2) - \tfrac{1}{9}\Delta\kappa H^2(3Q_H q + P_H p) \qquad (8)$$

if the field **H** is along one of the principal axes; here $Q_H = \frac{1}{2}(3\cos^2\theta_H - 1)$ and $P_H = \frac{3}{2}\sin^2\theta_H \cos 2\phi_H$ and θ_H and ϕ_H are the polar and azimuthal angles defining the orientation of **H**. Interchanging axes in a PAS gives rise to the group of transformations

$$\begin{bmatrix} q' \\ p' \end{bmatrix} = -\frac{1}{2}\begin{bmatrix} 1 & 1 \\ -3 & 1 \end{bmatrix}\begin{bmatrix} q \\ p \end{bmatrix} \quad \text{and}$$

$$\begin{bmatrix} q' \\ p' \end{bmatrix} = -\frac{1}{2}\begin{bmatrix} 1 & -1 \\ 3 & 1 \end{bmatrix}\begin{bmatrix} q \\ p \end{bmatrix}, \qquad (9)$$

ϵ(cos) is invariant under these transformations. In a PAS in the absence of a field. Eq. (7) has three distinct non-trivial solutions corresponding to alignment along the three principal axes. One of these solutions is uniaxial ($P = 0$) corresponding to alignment along the z-direction, while two are biaxial ($P \neq 0$) corresponding to alignment along the x- and y-directions. This set of solutions is invariant under the transformations of Eq. (9).

b. Binary Mixtures of Nematics

In a binary mixture of nematics consisting of N_1 molecules of species 1 and N_2 molecules of species 2 confined to a volume V, the single particle pseudopotential for molecules of type 1 (say) can be obtained by straightforward generalisation of Eq. (6). This gives

$$\begin{aligned}\epsilon_1(\hat{n}) = &-\tfrac{1}{2}\rho_1\gamma_{11} - \tfrac{2}{3}\rho_1 U_{11} S^{(1)}_{\alpha\beta}\sigma_{\beta\alpha} + \tfrac{1}{3}\rho_1 U_{11} S^{(1)}_{\alpha\beta} S^{(1)}_{\beta\alpha} \\ &-\tfrac{1}{2}\rho_2\gamma_{12} - \tfrac{2}{3}\rho_2 U_{12} S^{(2)}_{\alpha\beta}\sigma_{\beta\alpha} + \tfrac{1}{3}\rho_2 U_{12} S^{(2)}_{\alpha\beta} S^{(1)}_{\beta\alpha} \\ &-\tfrac{1}{3}\kappa_1 H_\alpha H_\beta \sigma_{\beta\alpha} \qquad (10)\end{aligned}$$

where the subscripts 1 and 2 and the superscripts (1) and (2) refer to species; thus γ_{ij} and U_{ij} are strengths of interactions between molecules of species i and j. The single particle pseudopotential for molecules of species 2 is obtained by interchanging indices in Eq.

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(10). The configurational free energy density of the system is

$$\mathcal{F} = -kT\rho_1 \ln \frac{1}{\rho_1} \int e^{-\beta\epsilon_1(\hat{n})}\, d^2\hat{n} - kT\rho_2 \ln \frac{1}{\rho_2} \int e^{-\beta\epsilon_2(\hat{n})}\, d^2\hat{n} \quad (11)$$

Minimising the free energy density with respect to $S^{(i)}_{\alpha\beta}$ $(i = 1,2)$ results in the self-consistent equations for the order parameters

$$S^{(i)}_{\alpha\beta} = \frac{\int \sigma_{\alpha\beta} e^{-\beta\epsilon_i(\hat{n})}\, d^2\hat{n}}{\int e^{-\beta\epsilon_i(\hat{n})}\, d^2\hat{n}}\,. \quad (12)$$

To investigate the possibility of coexisting phases, it is useful to evaluate the chemical potentials of the constituent species. Assuming the each molecule of species i has volume v_i and that $V = N_1 v_1 + N_2 v_2$, differentiation of the free energy with respect to particle number gives the chemical potential of species 1. That is,

$$\begin{aligned}\mu_1 = {} & -kT \ln \frac{1}{\rho_1} \int e^{-\beta\epsilon_1(\hat{n})}\, d^2\hat{n} + kT\rho_2(v_2 - v_1) \\ & - \frac{1}{2}\rho_2\left[\gamma_{11}\rho_1 v_2 - \gamma_{12}(\rho_1 v_1 - \rho_2 v_2) - \gamma_{22}\rho_2 v_1\right] \\ & - \frac{1}{3}\rho_2\left[U_{11}\rho_1 v_2 S^{(1)}_{\alpha\beta} S^{(1)}_{\beta\alpha} - U_{12}(\rho_1 v_1 - \rho_2 v_2) S^{(1)}_{\alpha\beta} S^{(2)}_{\beta\alpha}\right. \\ & \left. - U_{22}\rho_2 v_1 S^{(2)}_{\alpha\beta} S^{(2)}_{\beta\alpha}\right]. \quad (13)\end{aligned}$$

μ_2, the chemical potential of species 2, is obtained by interchanging indices in Eq. (13).

The equilibrium state of [a] binary mixture can now, in principle, be determined. For a single phase at a given temperature and composition the coupled self-consistent equations of Eq. (12) may be solved for $S^{(1)}_{\alpha\beta}$ and $S^{(2)}_{\alpha\beta}$; this allows the calculation of the free energy of the phase and of the chemical potentials of the two components. The equilibrium state of this phase corresponds to that solution for $S^{(1)}_{\alpha\beta}$ and $S^{(2)}_{\alpha\beta}$ of Eq. (12) which minimises the free energy. If two phases at the same temperature (but with different compositions) have the same chemical potential for each component, then the two phases may coexist; the equilibrium state of a single phase must therefore be determined for the entire range of compositions at a given temperature. The equilibrium state for the binary mixture at a given temperature and composition is therefore either a single phase or coexisting

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phases; the equilibrium configuration is the one which corresponds to the global minimum of the free energy.

In order to eliminate the solutions of the self-consistent equations for the order parameters (Eq. (12)) which are degenerate in the free energy, it is useful to work in a PAS. In the Appendix, it is shown that both order parameter tensors $S^{(1)}_{\alpha\beta}$ and $S^{(2)}_{\alpha\beta}$ are diagonal in the same PAS, and if a field **H** is present, it is along one of the principal axes. If the interaction strengths between different species in the pseudopotential obey the geometric mean assumption, that is, if $\gamma_{12} = \gamma_{21} = \sqrt{\gamma_{11}\gamma_{22}}$ and $U_{12} = U_{21} = \pm\sqrt{U_{11}U_{22}}$, the pseudopotential for species 1 becomes in this PAS,

$$\epsilon_1(\hat{n}) = -\frac{U_{11}}{v_1}\left[(A_1 + \delta_1 Q_H)q_1 + \frac{1}{3}(B_1 + \delta_1 P_u)p_1 - \frac{1}{2}A_1 Q_1 - \frac{1}{6}B_1 P_1 + \frac{1}{2}\frac{\gamma_{11}}{U_{11}}C_1\right] \tag{14}$$

where

$$A_1 = y_1 Q_1 + s\sqrt{\frac{U_{22}}{U_{11}}}\,\frac{v_1}{v_2}(1 - y_1)Q_2,$$

$$B_1 = y_1 P_1 + s\sqrt{\frac{U_{22}}{U_{11}}}\,\frac{v_1}{v_2}(1 - y_1)P_2,$$

$$C_1 = y_1 + \sqrt{\frac{\gamma_{22}}{\gamma_{11}}}\,\frac{v_1}{v_2}(1 - y_1),$$

$\delta_1 = \Delta\kappa_1 H^2 v_1/3U_{11}$, $s = \pm 1$, and $y_1 = N_1 v_1/(N_1 v_1 + N_2 v_2)$ is the volume fraction of component 1. The sign s of the anisotropic interspecies interaction term determines whether parallel or perpendicular alignment of molecules of different species is energetically favourable. If $s = +1$, the interspecies energy term $\sim s[3Q_i q_j + P_i p_j]$ is minimised if molecules of the two species align parallel to each other, while if $s = -1$ the energy is minimised if their alignment is perpendicular. The self-consistent equations for the order parameters become in this PAS

$$Q_1 = \frac{\int q e^{-\beta\epsilon_1(\hat{n})}\,d^2\hat{n}}{\int e^{-\beta\epsilon_1(\hat{n})}\,d^2\hat{n}} \quad \text{and} \quad P_1 = \frac{\int p e^{-\beta\epsilon_1(\hat{n})}\,d^2\hat{n}}{\int e^{-\beta\epsilon_1(\hat{n})}\,d^2\hat{n}}\,; \tag{15}$$

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here all four order parameters are coupled, since $\epsilon_i(\hat{n})$ is a function of Q_1, P_1, Q_2 and P_2. In the absence of a field, the isotropic configuration $Q_1 = Q_2 = P_1 = P_2 = 0$ always provides one solution, as does the uniaxial configuration $P_1 = P_2 = 0$. The chemical potential μ_1 for species 1 is given by

$$\frac{\mu_1}{kT} + \ln v_1 = \ln y_1 + (1 - y_1)\left(1 - \frac{v_1}{v_2}\right)$$
$$- \ln \int e^{(U_{11}/kTv_1)[(A_1 + \delta_1 Q_H)q + 1/3(B_1 + \delta_1 P_H)p + \gamma_{11}/U_{11}C_1]}\, d^2\hat{n}$$
$$+ \frac{1}{2}\,\frac{U_{11}}{kTv_1}\left[A_1^2 + \frac{1}{3}B_1^2 + \frac{\gamma_{11}}{U_{11}}C_1^2\right]. \tag{16}$$

Corresponding quantities for species 2 are obtained by interchanging indices in Eq's. (14–16); and $y_2 = 1 - y_1$.

If only a single phase is present, the free energy density of the system at a given temperature is

$$\mathscr{F} = \frac{y_1}{v_1}\,\mu_1 + \frac{y_2}{v_2}\,\mu_2 \tag{17}$$

where $\mu_1 = \mu_1(y_1)$ and $\mu_2 = \mu_2(y_2$. If two phases are present in say phase A and phase B with compositions y_{1B} and y_{1B} and chemical potentials $\mu_{1A} = \mu_{1B}$ and $\mu_{2A} = \mu_{2B}$, then the free energy density of the system of composition y_1 and y_2 is given by

$$\mathscr{F} = \frac{y_1}{v_1}\,\mu_{1A} + \frac{y_2}{v_2}\,\mu_{2A} \tag{18}$$

that is, the free energy density expression for the system is a linear interpolation between the free energy densities of the single phases A and B.

Now if two phases A and B coexist at a given temperature, the chemical potentials of each component in the two phases are equal. However, it is not straightforward in general to calculate the compositions y_{1A} and y_{1B} where this coexistence occurs. One method is to calculate the free energy density of the system as a function of composition y_1 using Eq. (17) assuming that only a single phase is present. At a given temperature and composition, each non-degenerate solution of the self-consistent equations (Eq. (15)) for the order parameters Q_1, Q_2, P_1 and P_2 gives rise to a corresponding free

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energy density; these values of the free energy density may be plotted as a function of composition y_1. Double tangent constructions to these free energy density curves (that is, the construction of straight lines which are tangent to the free energy density versus composition curves at two distinct points) identify the compositions where two-phase coexistence is possible. It is straightforward to show that the condition for the equality of the chemical potentials of each species in the two phases A and B with compositions y_{1A} and y_{1B} is that the straight line from the point $\{\mathscr{F}(y_{1A}), y_{1A}\}$ to the point $\{\mathscr{F}(y_{1B}), y_{1B}\}$ be tangent to the free energy density curve $\mathscr{F}(y_1)$ at both of these points. The doubly tangent straight line thus constructed corresponds to the expression of Eq. (18); however, two-phase coexistence will be realised only if this construction represents the lowest possible free energy of the system.

Since in general there are several solutions of the self-consistent equations for the order parameters and consequently several free energy density curves, the construction of all possible double tangents can become difficult, particularly if numerical rather than graphical methods are used. An alternate method to unambiguously locate possible two-phase regions is to examine the component activities. At a given temperature and composition, each non-degenerate solution of the self-consistent equations for the order parameters gives rise to a corresponding absolute activity $\lambda_1 = e^{\beta\mu_1}$ of species 1 and $\lambda_2 = e^{\beta\mu_2}$ of species 2. If λ_1 is plotted versus λ_2 for each of these order parameter solutions with composition a parameter along the curve, a set of activity curves is obtained. A curve may intersect with another curve or with itself; possible coexistence of two phases is indicated by these points of intersection. At such a point, two phases A and B with compositions y_{1A} and y_{1B} have the same activity and chemical potential for each component. These phases therefore coexist if the system can be decomposed into these phases, that is, if $y_{1A} < y_1 < y_{1B}$ where $y_{1A} < y_{1B}$, and if the corresponding free energy density given by Eq. (18) is the global minimum for this composition of the system.

Results and discussion

Phase diagrams for a number of binary systems were calculated using the theory outlined above. The pure constituent species are assumed to have nematic-isotropic transition temperatures T_{NI_1} and T_{NI_2}, molecular volumes v_1 and v_2 isotropic interaction strenghts γ_{11} and γ_{22} and anisotropic interaction strengths U_{11} and U_{22}. For simplicity, we have assumed that the interspecies interaction strengths are the geo-

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metric mean of the intraspecies terms, that is $\gamma_{12} = \gamma_{21} = \sqrt{\gamma_{11}\gamma_{22}}$ and $U_{12} = U_{21} = s\sqrt{U_{11}U_{22}}$. At a given temperature and composition y_1, the solutions of Eq. (15) were obtained by a method of successive iterations. The vector $[Q_1, Q_2, P_1, P_2]$ was initialised to each member of the set

$$\left[\left\{\begin{matrix} +1 \\ -\frac{1}{2} \\ 0 \end{matrix}\right\}, \left\{\begin{matrix} +1 \\ -\frac{1}{2} \\ 0 \end{matrix}\right\}, \left\{\begin{matrix} +\frac{3}{2} \\ -\frac{3}{2} \\ 0 \end{matrix}\right\}, \left\{\begin{matrix} +\frac{3}{2} \\ -\frac{3}{2} \\ 0 \end{matrix}\right\}\right];$$

substitution of this vector into the pseudopotentials of Eq. (14) generates the vector for the next step of the iteration. We have found that at high temperatures integrated series expansions of the exponentials in Eq. (15) were preferable to Gaussian quadrature; at low temperatures the opposite was the case. Once the order parameter iterations converged (to 1 part in 10^6), modified chemical potentials $\mu_1' = \mu_1/kT + \ln v_1$ and $\mu_2' = \mu_2/kT + \ln v_2$ were calculated using Eq. (16). The corresponding modified free energy density $\mathscr{F}' = y_1\mu_1' + y_2(v_1/v_2)\mu_2'$ was calculated together with the modified absolute activities $\lambda_1' = e^{\beta\mu_1'}$ and $\lambda_2' = e^{\beta\mu_2'}$. This procedure was repeated for different compositions, resulting in several order parameter, activity and free energy density curves at this temperature. Compositions of possibly coexisting phases were determined from intersections of activity curves. This enabled the evaluation of Eq. (18) for the free energy density in the two-phase region; this procedure was found to be more tractable than the equivalent double tangent method. The global minimum of this set of free energy density curves together with the corresponding order parameters was taken to correspond to the equilibrium configuration of the system.

The phase diagram for a previously reported[20] simple binary mixture is shown in Fig. 1a; the ratio of transition temperatures is $T_{NI_1}/T_{NI_2} = 2.5$ and the ratio of molecular volumes is $\nu_1/\nu_2 = 1.0$. The choice of relative isotropic interaction strengths $\gamma_{11}/\nu_1^2 = \gamma_{22}/\nu_2^2$ makes the system behaviour independent of the isotropic part of the interaction. The sign of the interspecies interaction term is $s = +1$; that is, the energetically favoured alignment of the two constituent species is parallel. The external field is zero. At temperatures between T_{NI_1} and T_{NI_2} the system may be composed of a coexisting uniaxial nematic and an isotropic phase. At low temperatures, two uniaxial nematic phases coexist. The order parameters along the coexistence curves are shown in Fig. 1b. It is worth noting that the order parameters of the two components are significantly different, the order

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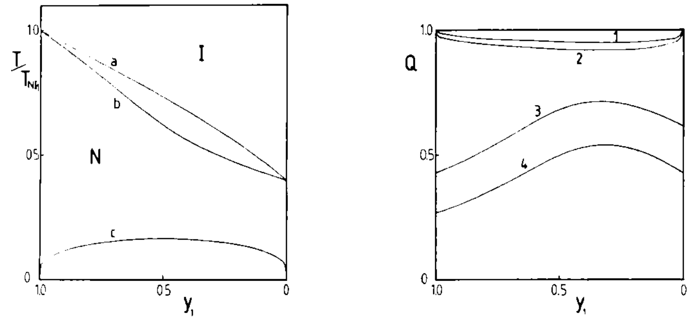
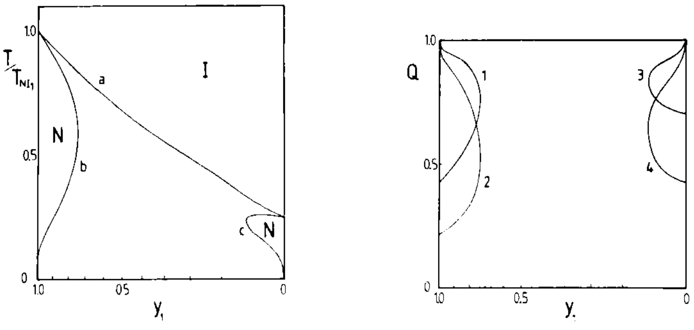


(a) (b)

FIGURE 1a Temperature-composition phase diagram for a binary nematic mixture with $T_{NI_1}/T_{NI_2} = 2.5$, $s = +1$ and $v_1/v_2 = 1.0$. Here $\gamma_{11}v_2^2/\gamma_{22}v_1^2 = 1.0$ and $H = 0$. y_1 is the volume fraction of species 1. The curves *a* and *b* are the nematic-isotropic coexistence curves; *c* is the nematic-nematic coexistence curve.

FIGURE 1b Component order parameters for the mixture of Fig. 1a. Curves 1 and 2 correspond to Q_1 and Q_2 along the nematic-nematic coexistence curve *c*, curves 3 and 4 correspond to Q_1 and Q_2 along the nematic-isotropic coexistence curve *b*. $P_1 = P_2 = 0$.

parameters of the pure components however follow the usual M-S behaviour. If the nematic-isotropic transition temperature of species 2 is further lowered, the two coexistence curves merge as shown on Fig. 2a. for $T_{NI_1}/T_{NI_2} = 4.0$. The corresponding order parameters are shown in Fig. 2b; the range of nematic composition is restricted to the edges of the phase diagram. The effects of the isotropic part of the potential are shown in Fig. 3a, where $\gamma_{11} = 3.5\ U_{11}$ and $\gamma_{22} =$



(a) (b)

FIGURE 2a Temperature-composition phase diagram for a binary nematic mixture with $T_{NI_1}/T_{NI_2} = 4.0$, $s = +1$ and $v_1/v_2 = 1.0$. Here $\gamma_{11}v_2^2/\gamma_{22}v_1^2 = 1.0$ and $H = 0$.

FIGURE 2b Component order parameters for the mixture of Fig. 2a. Curves 1 and 2 correspond to Q_1 and Q_2 along the coexistence curve *b*, curves 3 and 4 correspond to Q_1 and Q_2 along the coexistence curve *c*. $P_1 = P_2 = 0$. The scale on the volume fraction axis is non-linear.

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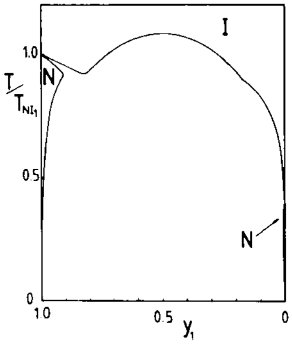
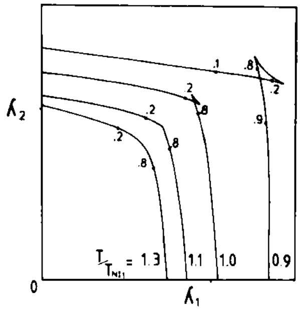


(a)



(b)

FIGURE 3a Temperature-composition phase diagram for a binary nematic mixture with $T_{NI_1}/T_{NI_2} = 2.5$, $s = +1$ and $\nu_1/\nu_2 = 1.0$. Here $\gamma_{11}/U_{11} = 3.5$, $\gamma_{22}/U_{22} = 2.0$, $\gamma_{11}\nu_2^2/\gamma_{22}\nu_1^2 = 4.375$ and $H = 0$.

FIGURE 3b Activity curves for the mixture of Fig. 3a at different temperatures, exhibiting a catastrophe. λ_1 and λ_2 are the modified activities in the isotropic phase of species 1 and 2 as defined in the text in arbitrary units. The parameter along each curve is y_1, the volume fraction of species 1.

2.0 U_{22} while $\gamma_{11}\nu_2^2/\gamma_{22}\nu_1^2 = 4.375$. The phase separation here is due to the dissimilarity of the isotropic interactions. Activity curves for this system are shown in Fig. 3b. As the temperature is lowered, the isotropic activity curves develop an elementary catastrophe and begin to cross back over themselves indicating phase separation into two coexisting isotropic phases. If the isotropic interactions for the two species become more similar, isotropic-isotropic coexistence disappears and phase separation occurs at lower temperatures, as shown in Fig. 4, where $\gamma_{11}\nu_2^2/\gamma_{22}\nu_1^2 = 2.5$.

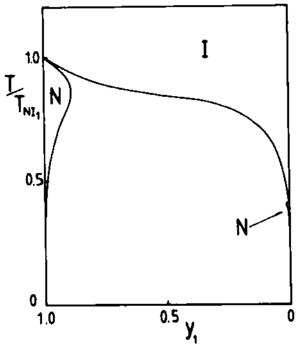


FIGURE 4 Temperature-composition phase diagram for a binary nematic mixture with $T_{NI_1}/T_{NI_2} = 2.5$, $s = +1$ and $\nu_1/\nu_2 = 1.0$. Here $\gamma_{11}/U_{11} = \gamma_{22}/U_{22} = 5.0$, $\gamma_{11}\nu_2^2/\gamma_{22}\nu_1^2 = 2.5$ and $H = 0$.

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It is interesting to examine the behaviour of systems where perpendicular alignment of the constituent species is energetically favourable; that is, if $s = -1$. The behaviour shown by such systems is expected to be similar to that of binary mixtures of hard rods and plates[13,15,21]. The phase diagram for a system with $T_{NI_1}/T_{NI_2} = 1.0$, $v_1/v_2 = 1.0$, $\gamma_{11}/v_1^2 = \gamma_{22}/v_2^2$ and $s = -1$ in the absence of a field is shown in Fig. 5a. The isotropic phase is separated from the uniaxial nematic phases U_+ and U_- by a two-phase region everywhere except at $y_1 = 1.0$, 0.5 and 0. For composition $y_1 > 0.5$, a uniaxial ($P_1 = P_2 = 0$) nematic phase U_+ with $Q_1 > 0$ and $Q_2 < 0$ exists below the $N - I$ transition, while for $y_2 < 0.5$, U_- with $Q_1 < 0$ and $Q_2 > 0$ occurs. These two phases coexist throughout most of the nematic temperature range; the order parameters along the coexistence curves are shown in Fig. 5b. A biaxial solution of the self-consistent order parameter equation does exist in the region indicated by the dashed lines in Fig. 5a, and it is lower in free energy than either uniaxial solution at the same composition. However, the free energy of the system in two coexisting uniaxial phases is still lower than that of the biaxial phase. The free energy densities corresponding to the various solutions are shown in Fig. 5c, for $T/T_{NI_1} = 0.7$, while the order parameters for the solutions which minimise the free energy at composition $y_1 = 0.76$ are shown in Fig. 5d. The biaxial phase B which undergoes a second order transition to the uniaxial phases $U_\pm$ is therefore seen to be precluded by phase separation. The dashed lines indicating the region where the biaxial solution exists correspond to the spinodal curve where $\partial^2\mathcal{F}/\partial y_1^2 = 0$ as indicated in Fig. 5c. Since in the spinodal region $\partial^2\mathcal{F}/\partial y_1^2 \leq 0$, the biaxial solution is unstable against fluctuations in composition, while the uniaxial solutions in the region between the $U_+ - U_-$ coexistence curve (binodal curve) and the dashed line spinodal curve are metastable. At the special point at composition $y_1 = 0.5$ all four phases I, U_+, U_- and B coexist but are indistinguishable. Rapid quenching of the isotropic fluid at this composition is expected to result in the formation of the biaxial phase, which, driven by material instability would then phase separate via spinodal decomposition. The effects of different transition temperatures and molecular volumes are shown in Fig. 6. For $T_{NI_1}/T_{NI_2} = 1.25$ and $v_1/v_2 = 0.75$; the topology of the phase diagram is unaltered by these changes.

Recently, experimental work has been carried out on binary nematic mixtures where the component susceptibilities had opposite signs.[25,26] We have calculated the phase behaviour of such a system for $T_{NI_1}/T_{NI_2} = 1.0$, $v_1/v_2 = 1.0$, $s = +1$, $\gamma_{11}/v_1^2 = \gamma_{22}/v_2^2$ $\delta_1 = +0$.

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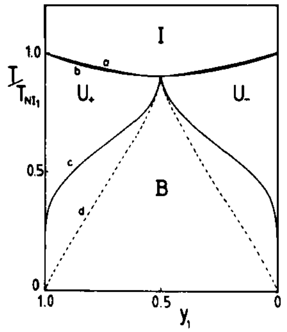
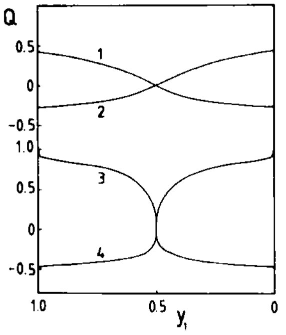
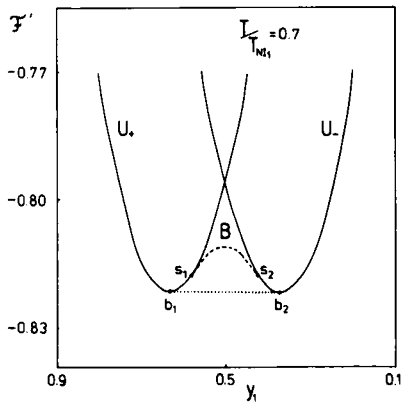


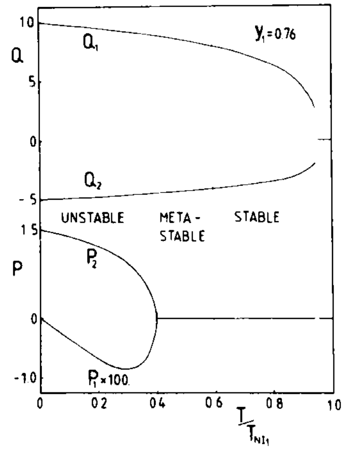
(a)



(b)



(c)



(d)

FIGURE 5a Temperature-composition phase diagram for a binary nematic mixture with T_{NI_1}/T_{NI_2}, = 1.0, $s = -1$ and $v_1/v_2 = 1.0$. Here $\gamma_{11}v_2^2/\gamma_{22}v_1^2 = 1.0$ and $H = 0$. The curves a and b are uniaxial nematic coexistence curves and d is the spinodal curve. The region where the biaxial solution exists is the spinodal region.

FIGURE 5b Component order parameters for the mixture of Fig. 5a. Curves 1 and 2 correspond to Q_1 and Q_2 along the coexistence curve 6, curves 3 and 4 correspond to Q_1 and Q_2 along the coexistence curve c. $P_1 = P_2 = 0$.

FIGURE 5c Modified free energy density F' as defined in the text in arbitrary units at temperature $T/T_{NI_1} = 0.7$ for the mixture of Fig. 5a. The uniaxial solutions are shown with solid lines, the biaxial solution with the dashed line and the double tangent construction with the dotted line. b_1 and b_2 are the binodal points, while s_1 and s_2 are the spinodal points.

FIGURE 5d Order parameter solution for the mixture of Fig. 5a as function of temperature at the composition $y_1 = 0.76$. For temperatures below $T/T_{NI_1} = 0.4$, the solution is unstable. For $0.4 < T/T_{NI_1} < 0.6$, the solution is metastable, while for $T/T_{NI_1} > 0.6$ it is stable.

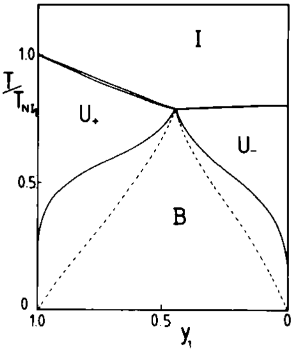
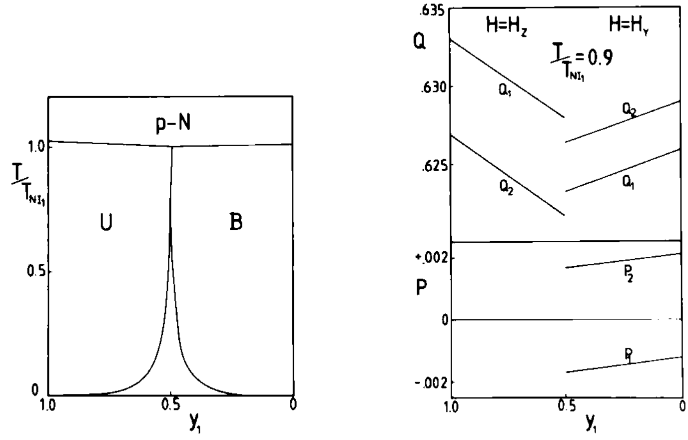


FIGURE 6 Temperature-composition phase diagram for a binary mixture with $T_{NI_1}/T_{NI_2} = 1.25$, $s = -1$ and $v_1/v_2 = 1.0$. Here $\gamma_{11}v_2^2/\gamma_{22}v_1^2 = 1.0$ and $H = 0$.

005 and $\delta_2 = -0.005$ where $\delta = \Delta\kappa H^2 v_1/3U_{11}$; the phase diagram is shown in Fig. 7a. Below the nematic (N)—paranematic ($p-N$) transition, a uniaxial (U) phase ($Q_1>0$, $Q_2>0$) coexists with a biaxial ($Q_1<0$, $Q_2>0$, $P_1,P_2 \neq 0$) (B) phase if the applied field **H** is along the z-axis. The order parameters at $T/T_{NI_1} = 0.9$ are shown as functions of composition y_1 in Fig. 7b. For $y_1>0.5$, the field is along the



(a) (b)

FIGURE 7a Temperature-composition phase diagram for a binary nematic mixture with $T_{NI_1}/T_{NI_2} = 1.0$, $s = +1$ and $v_1/v_2 = 1.0$. Here $\gamma_{11}v_2^2/\gamma_{22}v_1^2 = 1.0$ while $\Delta\kappa_1 H^2 v_1/3U_{11} = +0.005$ and $\Delta\kappa_2 H^2 v_2/3U_{22} = -0.005$. $p-N$ refers to the paranematic phase.

FIGURE 7b Order parameters for the mixture of Fig. 7a. at temperature $T/T_{NI_1} = 0.9$ showing first order uniaxial-biaxial transition. For $y_1 > 0.5$ $H = H_z$, while for $y_1 < 0.5$ $H = H_y$.

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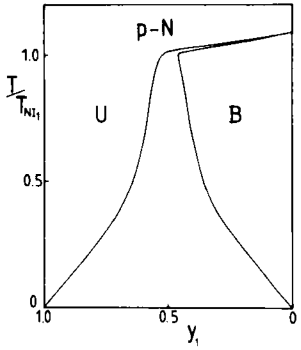

FIGURE 8 Temperature-composition phase diagram for a binary nematic mixture with $T_{NI1}/T_{NI2} = 1.0$, $s = +1$ and $\nu_1/\nu_2 = 1.0$. Here $\gamma_{11}\nu_2^2/\gamma_{22}\nu_1^2 = 1.0$ while $\Delta\kappa_1 H^2\nu_1/3U_{11} = +0.05$ and $\Delta\kappa_2 H^2\nu_2/3U_{22} = -0.05$. There is no uniaxial nematic-paranematic transition; the biaxial nematic-paranematic transition is still first order.

z-axis, while for $y_1 < 0.5$, a coordinate transformation has been made such that **H** is along the y-axis. This transformation has been carried out to show the least change in the order parameters across the transition, which is seen to be first order. The nematic-paranematic transitions $U - p-N$ and $B - p-N$ are also first order at this field strength; however, the two-phase region is too narrow to be visible on the diagram. For the pure components, as the field **H** is increased, the $U - p-N$ transition disappears above a critical value of the field[23] and above a second (higher) critical value, the $B - p-N$ transition becomes second order. The phase diagram at a field strength between these two critical values is shown in Fig. 8, where $\delta_1 = +0.05$ and $\delta_2 = -0.05$.

CONCLUSIONS

A rotationally invariant generalisation of the M-S pseudopotential has been extended to binary mixtures of nematics. Minimisation of the resulting free energy of the system leads to self-consistent equations for the component order parameter tensors. We have shown that both order parameter tensors are diagonal in the same principal axis frame, and if a field is applied, it is along one of these principal axes. The uniaxial and biaxial order parameters in this frame may be evaluated by a simple iterative process, enabling the calculation of the chemical potentials and absolute activities of the components. A simple method is proposed for determining two-phase coexistence and the phase diagram.

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In general, the component order parameters are significantly different in a given phase, although order parameters of the pure components follow the usual M-S behaviour. Binary mixtures of simple nematics which prefer to align parallel to each other show coexisting uniaxial nematic-isotropic and uniaxial nematic-uniaxial nematic phases. If the isotropic interaction is different for the two components, phase separation similar to that observed in isotropic binary fluids is obtained. In mixtures of nematics which prefer to align perpendicular to each other a solution corresponding to a biaxial phase exists; this phase is similar to that predicted by lattice,[13] hard particle[15] and van der Waals theories.[21] We have shown however that for the systems studied this solution is unstable since it coincides with the spinodal region: rapid quenching of such a system is predicted to exhibit spinodal decomposition. Mixtures of similar materials but with opposite signs of the susceptibility show coexisting uniaxial and biaxial phases in the presence of a field; the magnitude of the field can affect the order of the transitions and the topology of the phase diagram.

The extension of the simple M-S theory to mixtures outlined above predicts a rich variety of phase behaviour; some of these predictions are in fair agreement with experiment.[3,22] Detailed comparison is made difficult by the fact that pure nematics do not obey the predictions of the M-S theory exactly. Work to explicitly include steric effects and the smectic interaction in the pseudopotential are currently under way.

Acknowledgements

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APPENDIX

In a single phase of a binary nematic mixture in a magnetic field **H**, the free energy density is

$$\mathcal{F} = -kT\rho_1 \ln \frac{1}{\rho_1} \int e^{-\beta\epsilon_1(\hat{n})}\, d^2\hat{n} - kT\rho_2 \ln \frac{1}{\rho_2} \int e^{-\beta\epsilon_2(\hat{n})}\, d^2\hat{n} \qquad \text{(A1)}$$

where $\epsilon_1(\hat{n})$ and $\epsilon_2(\hat{n})$ are given by Eq. (10). This expression is independent of choice of coordinate systems; we choose the coordinate system where the tensor $\Delta\kappa_1\rho_1 S^{(1)}_{\alpha\beta} + \Delta\kappa_2\rho_2 S^{(2)}_{\alpha\beta}$ is diagonal. We

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wish to determine in this coordinate system the direction of **H** which minimises $\mathcal{F}$. We require therefore the minimum of $\mathcal{F}$ with respect to the components H_α subject to the constraint that H is fixed; that is, the free minimum of $\mathcal{F} + \eta(H_x^2 + H_y^2 + H_z^2)$ where η is a Lagrange multiplier. This gives at once

$$(\Delta\kappa_1\rho_1 S_{xx}^{(1)} + \Delta\kappa_2\rho_2 S_{xx}^{(2)})H_x = 3\eta H_x \tag{A2}$$

and similarly for y and z. Multiplying these equations by H_x, H_y and H_z respectively and adding gives

$$\begin{aligned}&\rho_1\Delta\kappa_1\left[H_x^2 S_{xx}^{(1)} + H_y^2 S_{yy}^{(1)} + H_z^2 S_{zz}^{(1)}\right]\\ &+ \rho_2\Delta\kappa_2\left[H_x^2 S_{xx}^{(2)} + H_y^2 S_{yy}^{(2)} + H_x^2 S_{zz}^{(2)}\right] = 3\eta H^2\end{aligned} \tag{A3}$$

Solving for η and substituting into Eq. A2 gives

$$\begin{aligned}&H_x H^2\left[\Delta\kappa_1\rho_1 S_{xx}^{(1)} + \Delta\kappa_2\rho_2 S_{xx}^{(2)}\right]\\ &= H_x\rho_1\Delta\kappa_1\left[H_x^2 S_{xx}^{(1)} + H_y^2 S_{yy}^{(1)} + H_z^2 S_{zz}^{(1)}\right]\\ &+ H_x\rho_2\Delta\kappa_2\left[H_x^2 S_{xx}^{(2)} + H_y^2 S_{yy}^{(2)} + H_z^2 S_{zz}^{(2)}\right]\end{aligned} \tag{A4}$$

and similarly for y and z. Solutions of Eq. (A4) are $H_x = 0$ or $H_y = H_z = 0$ and similarly for y and z. Thus F is an extremum if **H** is along one of the axes of the frame where $\Delta\kappa_1\rho_1 S_{\alpha\beta}^{(1)} + \Delta\kappa_2\rho_2 S_{\alpha\beta}^{(2)}$ is diagonal.

Next we wish to show that in the absence of a field **H**, $S_{\alpha\beta}^{(1)}$ and $S_{\alpha\beta}^{(2)}$ are diagonal in the same frame. Due to the orthogonality of spherical harmonics, if

$$S_{\alpha\beta} = c\int \sigma_{\alpha\beta} e^{\Lambda_{\alpha\beta}\sigma_{\beta\alpha}} d^2\hat{n} \tag{A5}$$

where $\Lambda_{\alpha\beta}$ is an arbitrary tensor (with constant elements) and c is a constant, if $\Lambda_{\alpha\beta}$ is diagonal, $S_{\alpha\beta}$ is also diagonal. It follows from Eq. (10) that in general, if $\mathbf{H} = 0$,

$$S_{\alpha\beta}^{(1)} = c\int \sigma_{\alpha\beta} e^{(2/3kT)[\rho_1 U_{11} S_{\alpha\beta}^{(1)} + \rho_2 U_{22} S_{\alpha\beta}^{(2)}]\sigma_{\beta\alpha}} d^2\hat{n} \tag{A6}$$

where c is a normalisation constant. In the frame where $\rho_1 U_{11} S_{\alpha\beta}^{(1)} + \rho_2 U_{22} S_{\alpha\beta}^{(2)}$ is diagonal, $S_{\alpha\beta}^{(1)}$ is also diagonal and so is $S_{\alpha\beta}^{(2)}$.

In the absence of a field, the tensors $S_{\alpha\beta}^{(1)}$, $S_{\alpha\beta}^{(2)}$ and $\Delta\kappa_1\rho_1 S_{\alpha\beta}^{(1)} + \Delta\kappa_2\rho_2 S_{\alpha\beta}^{(2)}$ are all diagonal in the same PAS. If a field **H** is applied along one of the principal axes, the PAS will not undergo a rotation with respect to the field direction since the free energy is already an extremum, and since this field does not introduce off-diagonal elements into the pseudopotentials, $S_{\alpha\beta}^{(1)}$ and $S_{\alpha\beta}^{(2)}$ will remain diagonal. Thus, in general, both order parameter tensors are diagonal in the same principal axis frame, and if a single field is applied, it will be along one of the principal axes.

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