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Phase diagrams of binary mixtures of biaxial nematogens

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A mean field theory is used to describe nematic phases of binary mixtures of biaxial molecules. Using a general pseudopotential consistent with the D_{2h} symmetry of the constituent particles, the theory is used to calculate the elements of the order tensors necessary to describe the orientational order in binary mixtures in both uniaxial and biaxial nematic phases. For a single component, the model only requires one parameter, r_2, a ratio of anisotropic interaction strengths, to predict the temperature dependence of the four order parameters. The temperature dependence of the orientational distribution functions is illustrated for both rod-like and plate-like molecules. For binary mixtures, three anisotropic interaction strengths, r_1, r_2, and r_3, are needed to calculate the order parameters of both components as a function of concentration and temperature. The free energy is evaluated to predict the phase stability of the mixture. By systematically varying the anisotropic interaction strengths, temperature–concentration phase diagrams for a variety of molecular shapes are presented. The theoretical predictions suggest that binary mixtures of molecules with highly asymmetric shapes will display stable biaxial nematic phases.

1. Introduction

Mean field theories which predict the temperature dependence of orientational ordering in liquid crystals have a thirty year history. The well-known Maier–Saupe theory [1] assumed a uniaxial nematic phase (N_U) of cylindrically symmetric particles. Ten years later, this formalism was extended to describe particles lacking an axis of rotational symmetry [2–4]. These generalizations predicted biaxial phases (N_B) ten years before they were discovered in lyotropics [5] and fifteen years before the first reports of thermotropic biaxial nematogens surfaced [6–8]. Presently, there is considerable doubt if the existence of a thermotropic biaxial phase has been proven unambiguously [9, 10]. Characteristics of the nematic phase have been investigated using a variety of descriptions: other mean field theories [11], lattice models [12–14], biaxial Onsager-type theories [15], Landau approaches [3], and Monte Carlo molecular dynamics simulations of hard ellipsoids [16]. For single component systems, all these models come to the same conclusion: the phase behaviour depends on the shape of the molecules. For both prolate (rod-like) and oblate (plate-like) liquid crystal molecules, any deviation from cylindrical symmetry results in a second order phase transition from the uniaxial nematic phase to the biaxial nematic phase as the temperature is lowered. For some critical value of molecular shape anisotropy, this N_B–N_U phase transition temperature, T_{BU}, becomes equal to the N_U–I transition

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temperature, T_{NI}. These calculations suggest that designing a mesogen which combines the features of both rods and disks might result in a low molecular weight biaxial nematic [17].

Theoretical predictions for the behaviour of binary mixtures of nematogens are extremely model dependent. Some mean field lattice models [12, 18], extended Onsager theories [19, 20] and mean field van der Waals-type theories [21] have predicted that mixtures of rod-like and disk-like nematogens should produce biaxial nematic phases. Conversely, both molecular mean field theories, in which interactions between particles satisfy the geometric mean rule [22, 23], and a Monte Carlo simulation of mixtures of rods and disks [24] predict that these binary mixtures will phase separate into two uniaxial phases. This latter prediction is consistent with the lack of experimental evidence for biaxial phases in mixtures of rod-like and plate-like molecules.

Recently a mean field theory has been proposed [25] which includes both molecular and phase biaxiality. This approach uses a geometric mean assumption to simplify the pseudopotential [22, 23, 25–28]. The result is a theory which requires one parameter (r_2) to predict the temperature dependence of (both biaxial and uniaxial) order parameters of a single component nematic, and three parameters (r_1, r_2, r_3) to describe the temperature and concentration dependence of orientational order in a binary mixture. These parameters are ratios of anisotropic interaction strengths describing the coupling of the molecular orientation to the mean field with r_2 and r_3 increasing as the biaxiality of the molecules increases. The temperature dependences of the two order parameters (Q and D) of biaxial particles in a uniaxial phase have been described before [29, 30] and construction of temperature–concentration phase diagrams of mixtures has been used to illustrate the stability of biaxial phases in mixtures of cylindrically symmetric molecules [22, 23]. The goal of the present work is to predict, for the first time, the temperature dependence of all four second rank order parameters of a biaxial nematogen and to observe the effect of molecular biaxiality on the symmetry of the nematic phase. The first section of this paper presents calculations of the pseudopotentials, order parameters, free energies, average energy densities, and chemical potentials which are needed to describe the system and evaluate phase stability. The second section presents the results of the calculations. The temperature dependences of the four order parameters describing alignment of a single component biaxial nematogen in a biaxial phase are presented and interpreted. Temperature–concentration phase diagrams of binary mixtures of a variety of liquid crystal mixtures are presented. In the conclusion, these results are compared to both experimental findings [6–10] and predictions of other theoretical descriptions [1–4, 11–30].

2. Analysis

The second rank order parameters which completely characterize orientational order of biaxial particles (D_{2h} symmetry) [2] are presented below:

$$Q=\tfrac{1}{2}\langle 3\cos^2(\theta)-1\rangle=\langle q\rangle, \tag{1}$$

$$D=-\tfrac{3}{2}\langle \sin^2(\theta)\cos(2\psi)\rangle=\langle d\rangle, \tag{2}$$

$$P=-\tfrac{3}{2}\langle \sin^2(\theta)\cos(2\phi)\rangle=\langle p\rangle, \tag{3}$$

$$\begin{aligned} C=\tfrac{3}{2}\langle &(1+\cos^2(\theta))\cos(2\phi)\cos(2\psi) \\ &-2\cos(\theta)\sin(2\phi)\sin(2\psi)\rangle=\langle c\rangle. \end{aligned} \tag{4}$$

The angles (ϕ, θ, ψ) are x-convention Euler angles [31] which describe the rotation from the laboratory fixed frame into the molecule fixed frame and $\langle \ \rangle$ denotes an ensemble average. By using the geometric mean assumption [22, 23, 25–28], a general mean field pseudopotential with 13 independent coupling constants is reduced to a form in which all particles feel the same isotropic (Γ), uniaxial nematic (Λ), and biaxial nematic (Λ') mean fields [25]. The resulting pseudopotentials, ε_i, for both components of the binary mixture $(i=1,2)$ are functions of the eight scalar order parameters (Q_i, D_i, P_i, C_i) and the three Euler angles (ϕ, θ, ψ).

$$\begin{aligned}\varepsilon_1 = &-\tfrac{3}{2}\Lambda[q_1(\theta)+r_2 d_1(\theta,\psi)-\tfrac{1}{2}Q_1-\tfrac{1}{2}r_2 D_1]\\ &-\tfrac{3}{2}\Lambda'[p_1(\phi,\theta)+r_2 c_1(\phi,\theta,\psi)-\tfrac{1}{2}P_1-\tfrac{1}{2}r_2 C_1]-\tfrac{1}{2}\Gamma.\end{aligned} \tag{5}$$

$$\begin{aligned}\varepsilon_2 = &-\tfrac{3}{2}\Lambda[r_1 q_2(\theta)+r_3 d_2(\theta,\psi)-\tfrac{1}{2}r_1 Q_2-\tfrac{1}{2}r_3 D_2]\\ &-\tfrac{3}{2}\Lambda'[r_1 p_2(\phi,\theta)+r_3 c_2(\phi,\theta,\psi)-\tfrac{1}{2}r_1 P_2-\tfrac{1}{2}r_3 C_2]-\tfrac{1}{2}r_0\Gamma.\end{aligned} \tag{6}$$

Where the mean fields $(\Gamma, \Lambda, \Lambda')$ are concentration dependent (functions of the number densities, ρ_1 and ρ_2), and are scaled by the isotropic (γ_{11}) and the uniaxial (U_{11}) interaction strengths for particle 1, specifically

$$\Gamma=\gamma_{11}(\rho_1+r_0\rho_2), \tag{7}$$

$$\Lambda=\tfrac{2}{3}U_{11}(\rho_1 Q_1+r_1\rho_2 Q_2+r_2\rho_1 D_1+r_3\rho_2 D_2), \tag{8}$$

$$\Lambda'=\tfrac{2}{9}U_{11}(\rho_1 P_1+r_1\rho_2 P_2+r_2\rho_1 C_1+r_3\rho_2 C_2). \tag{9}$$

Different molecules vary in their ability to couple to these fields, and the parameters of the mean field theory, r_0, r_1, r_2 and r_3, are functions of these coupling strengths.

$$r_0=\sqrt{\left(\frac{\gamma_{22}}{\gamma_{11}}\right)},\quad r_1=\sqrt{\left(\frac{U_{22}}{U_{11}}\right)},\quad r_2=\sqrt{\left(\frac{W_{11}}{U_{11}}\right)},\quad r_3=\sqrt{\left(\frac{W_{22}}{U_{11}}\right)}. \tag{10}$$

The constant U_{ii} measures the strength of the interaction coupling the instantaneous orientation of the major axis of the species i to the mean fields. W_{ii} gives a measure of the interaction strength coupling the instantaneous orientation of the minor axis of species i to the means fields, and γ_{ii} gives the isotropic coupling strength.

Statistical mechanics is used to calculate the order parameters. The single particle partition function for the ith species (Z_i) and the order parameters $(\xi_i=Q_i, D_i, P_i, C_i)$ may be calculated for both species, i, by evaluating the integrals

$$Z_i=\int \exp\left(-\frac{\varepsilon_i(\phi,\theta,\psi)}{k_B T}\right)\sin(\theta)\,d\phi\,d\theta\,d\psi, \tag{11}$$

$$\langle\xi_i\rangle=\frac{\int \xi_i \exp\left(-\frac{\varepsilon_i(\phi,\theta,\psi)}{k_B T}\right)\sin(\theta)\,d\psi\,d\theta\,d\phi}{Z_i}. \tag{12}$$

Since the pseudopotentials are simply functions of the uniaxial and biaxial order parameters of both species, this set of equations can be iterated until it converges to give self consistent solutions for all eight orientational order parameters.

The ϕ dimension of the integral in equations (11) and (12) was performed analytically. The remaining two-dimensional forms of the five integrals given in terms of spherical Bessel functions are presented in the Appendix. In the case of a uniaxial phase, the integrands are independent of the angle ϕ, and in this case the integration over the angle ψ can be performed analytically. Romberg's method was employed [32] to evaluate the ten two-dimensional integrals required for each iteration in the order parameter calculation for biaxial phases. The spherical Bessel functions were calculated using a polynomial expansion [33] which gave absolute errors of less than one part in 10^7. The convergence criterion for integration in the Θ dimension required fractional accuracy of less that 10^{-6}; the second dimension, ψ, required fractional errors of less that one part in 10^5. The order parameters themselves are reiterated until they are consistent to within one part in 10^4. The integrals were checked for a test case by comparison to Mathematica's [34] numerical result of evaluating the actual three dimensional integrals, and the solution was found to be correct to within the errors cited. Since this theory reduces to a previously published uniaxial model [22] when molecular biaxiality is ignored ($D=C=0$), the numerics also were checked by reproducing the phase diagrams presented in that work. Further verifications included comparing the temperature dependence of the order parameters Q and D, calculated for prolate molecules in a uniaxial phase ($\mathrm{N}_{\mathrm{U}+}$), with previously published results (r_2 is equal to δ in [30]), and reproducing the results of Maier and Saupe for a uniaxial, single component system [1] when $r_1=r_2=r_3=0$.

Once the order parameters have converged, the configurational free energy density of the homogeneous mixture can be calculated

$$f=\frac{F}{k_{\mathrm{B}}TV}=-\rho_1\ln\left[\frac{1}{\rho_1}Z_1\right]-\rho_2\ln\left[\frac{1}{\rho_2}Z_2\right]. \tag{13}$$

Other thermodynamic quantities of interest which were calculated include the thermal average energy densities $\langle\varepsilon_1\rangle$, $\langle\varepsilon_2\rangle$ and the entropy density σ,

$$\langle\varepsilon_1\rangle=\langle\alpha\rangle\rho_1+\langle\beta\rangle\rho_2, \tag{14}$$

$$\langle\varepsilon_2\rangle=\langle\alpha'\rangle\rho_1+\langle\beta'\rangle\rho_2, \tag{15}$$

$$\frac{\sigma}{k_{\mathrm{B}}TV}=\langle\alpha\rangle, \tag{16}$$

where

$$\langle\alpha\rangle=-\frac{U_{11}}{2}(Q_1+r_2D_1)^2-\frac{U_{11}}{6}(P_1+r_2C_1)^2-\frac{\gamma_{11}}{2}, \tag{17}$$

$$\begin{aligned}\langle\beta\rangle=\langle\alpha'\rangle=&-\frac{U_{11}}{2}(Q_1+r_2D_1)(r_1Q_2+r_3D_2)\\&-\frac{U_{11}}{6}(P_1+r_2C_1)(r_1P_2+r_3C_2)-r_0\frac{\gamma_{11}}{2},\end{aligned} \tag{18}$$

$$\langle\beta'\rangle=-\frac{U_{11}}{2}(r_1Q_2+r_3D_2)^2-\frac{U_{11}}{6}(r_1P_2+r_3C_2)^2-r_0^2\frac{\gamma_{11}}{2}. \tag{19}$$

For a pure component, if the entropy density jumps discontinuously at the transition, i.e. there is a finite entropy of transition, then the phase change is first order [35]. For second order transitions, the entropy changes continuously through the transition.

For homogeneous mixtures, the chemical potential, μ_i, can be calculated for all components. This chemical potential is crucial for calculating temperature–

concentration phase diagrams, since coexistence regions occur where the component chemical potentials are equal. For a binary mixture,

$$\mu_1=\frac{\partial F}{\partial N_1}=-k_{\mathrm{B}}T\ln\left[\frac{1}{\rho_1}Z_1\right]+k_{\mathrm{B}}T\rho_2(v_2-v_1)$$

$$+\rho_2[\rho_1v_2\langle\alpha\rangle+(p_2v_2-\rho_1v_1)\langle\beta\rangle-\rho_2v_1\langle\beta'\rangle], \qquad (20)$$

$$\mu_2=\frac{\partial F}{\partial N_2}=-k_{\mathrm{B}}T\ln\left[\frac{1}{\rho_2}Z_2\right]+k_{\mathrm{B}}T\rho_1(v_1-v_2)$$

$$-\rho_1[\rho_1v_2\langle\alpha\rangle+(\rho_2v_2-\rho_1v_1)\langle\beta\rangle-\rho_2v_1\langle\beta'\rangle] \qquad (21)$$

where v_i is the molecular volume or the *i*th species.

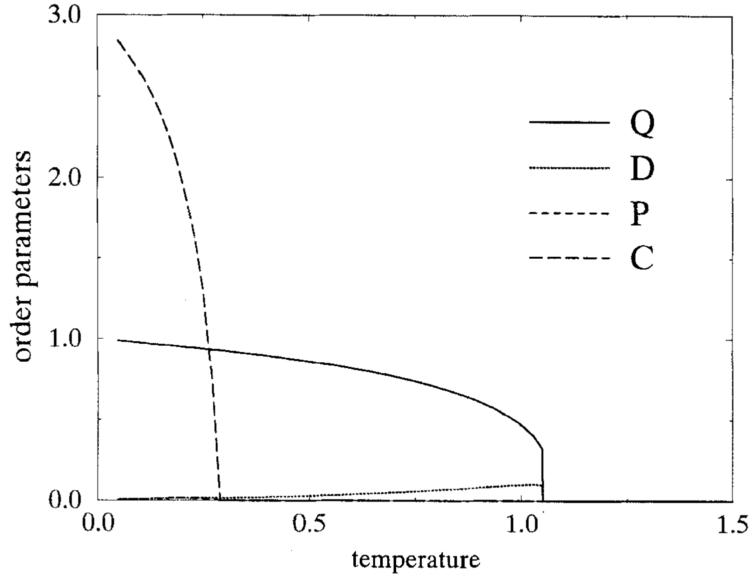
For studying orientational order of a single component system only the ratio of the biaxial coupling strength to the uniaxial coupling strength, r_2, is needed. Given this parameter, the temperature dependence of the order parameters can be calculated assuming a biaxial phase ($\mathrm{N_B}$), a uniaxial phase of prolate molecules (rods) with $Q>0$ ($\mathrm{N_{U+}}$), or a uniaxial phase of oblate molecules (plates) having $Q<0$ ($\mathrm{N_{U-}}$). Obviously, the biaxial order parameters, P and C, are zero in a uniaxial phase. When calculating the uniaxial order parameters, the algorithm converged to whichever solution was closest to the initial conditions for the order parameters. In the biaxial phase, it was found that the self-consistent equations converged to the same orientational distribution independent of initial order parameter guess; however, the principle axis from which the Euler angles were defined depends on the initial conditions for the order parameters. For all phases, the scaled free energy density is calculated for a single component using equation (13) with $\rho_2=0$. The phase having the minimum orientational free energy gives the equilibrium state of the system. Predictions for the temperature dependence of the four order parameters (Q, D, P, C) as functions of molecular biaxial coupling strength, r_2, are presented in the results section.

For binary mixtures, phase separation occurs when the combined free energy of the separated phases is lower than the free energy of the homogeneous mixture. Temperature–composition phase diagrams give the concentrations and temperatures where these miscibility gaps occur [22, 23, 35]. It is of interest to calculate phase diagrams of different mixtures of molecules with a variety of uniaxial and biaxial coupling strengths. For a given temperature, once the free energy of a homogeneous mixture is known as a function of composition (equation (13)), the minimum free energy phase of the system can be determined. If any line connecting two points on the homogeneous free energy curves lie below it, the composition range between the two points is unstable and phase separation will occur. The most stable configuration can be found by constructing a double tangent to the homogenous free energy curves. An equivalent method for finding this double tangent involves the calculation of the chemical potential of both components (equations (20) and (21)) [22, 35]. When the chemical potentials of both components, μ_i, are equal, the phases are in thermal and diffusive equilibrium and can coexist. Therefore, the concentrations where the chemical potentials are equal gives the location of the miscibility gaps. Plotting the chemical potentials μ_1 against μ_2 and locating the point where the curve crosses itself gives a second, more numerically efficient method of determining coexistence regions. Phase diagrams for a number of mixtures are presented in the results and discussion section. In producing the temperature–concentration phase diagrams, the volumetric fraction (Y) will be given in lieu of the number density (see the Appendix). In all phase diagrams presented, the volume per molecule and the isotropic interaction strength are set equal for both components to emphasize the effect of the anisotropic interaction strengths.

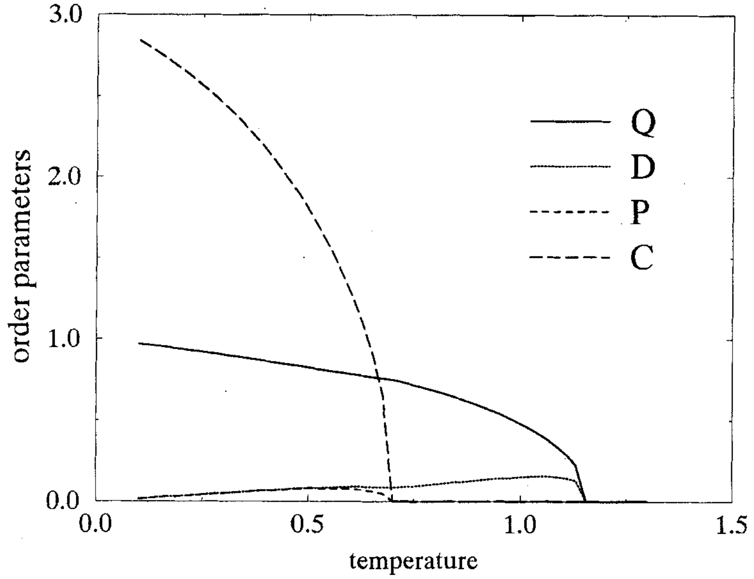
3. Results and discussion

First, the mean field theory prediction for the temperature dependence of all order parameters (Q, D, P, C) for a pure component was investigated. The temperature dependences of these order parameters are presented for five different values of the biaxial coupling parameter, r_2, in figure 1. At each given temperature, equations (11) and (12) were iterated to calculate the four order parameters. Depending on initial conditions and phase symmetry, four solutions were found: a biaxial solution (N_B), a uniaxial solution with $Q>0$ (N_{U+}), a uniaxial solution with $Q<0$ (N_{U-}) and an isotropic solution (I). The equilbrium solution for the system was taken to be that of minimum free energy (equation (13)). Small values of r_2 ($r_2<0{\cdot}33$) describe rod-like or prolate molecules, while for $r_2=0$ the rods are cylindrically symmetric and the Maier–Saupe results [1] are reproduced. Large values of r_2 ($r_2>0{\cdot}33$) describe plate-like or oblate molecules, with r_2 larger than 1·0 describing nearly cylindrically symmetric plates. The biaxial phase is found near the transition temperature (T_{NI}) for intermediate values of r_2 ($r_2\approx0{\cdot}33$). This is in agreement with previous work [2–4, 11–16] which predicted that low molecular weight thermotropic biaxial nematic liquid crystals should display characteristics of both rod-like and disk-like molecular shapes [10, 17].

As the temperature is lowered, mean field theory predicts that nematic liquid crystals become more ordered following the sequence I–N_{U+}–N_B (rods) or I–N_{U-}–N_B (disks). The entropy of transition was calculated using equation (16) and the results indicate that the phase transition from the isotropic phase ($Q=D=P=C=0$) to the uniaxial nematic phases ($P=C=0$) is first order. The entropy of transition between the isotropic phase and the uniaxial nematic phase decreased as the molecular biaxiality parameter approached $r_2=0{\cdot}33$ from either above (I–N_{U-}) or below (I–N_{U+}). The



(a)


3.0
2.0
1.0
0.0
0.0
0.5
1.0
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order parameters
temperature
Q
D
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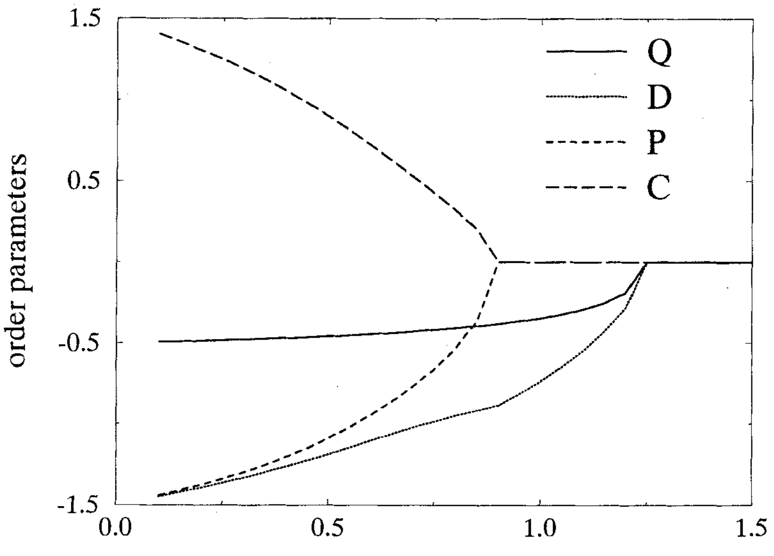
C

(*b*)


1.5
0.5
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-1.5
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1.5
order parameters
temperature
Q
D
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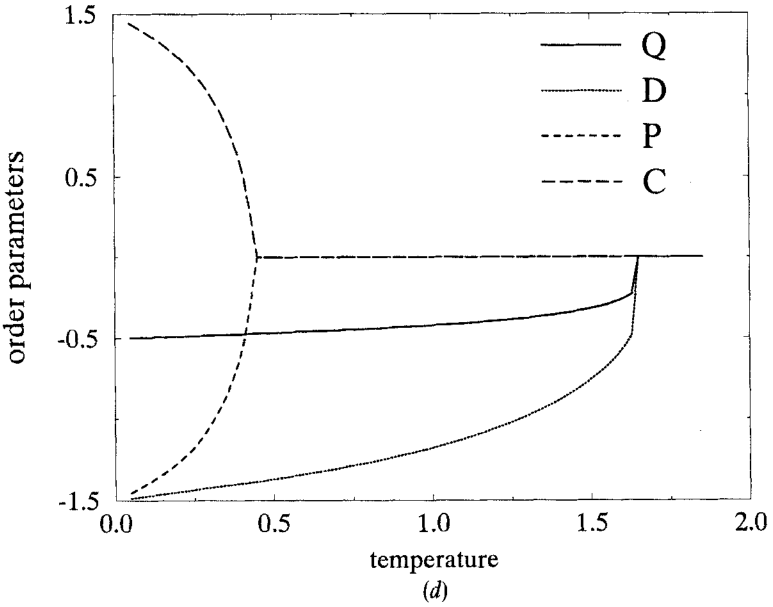

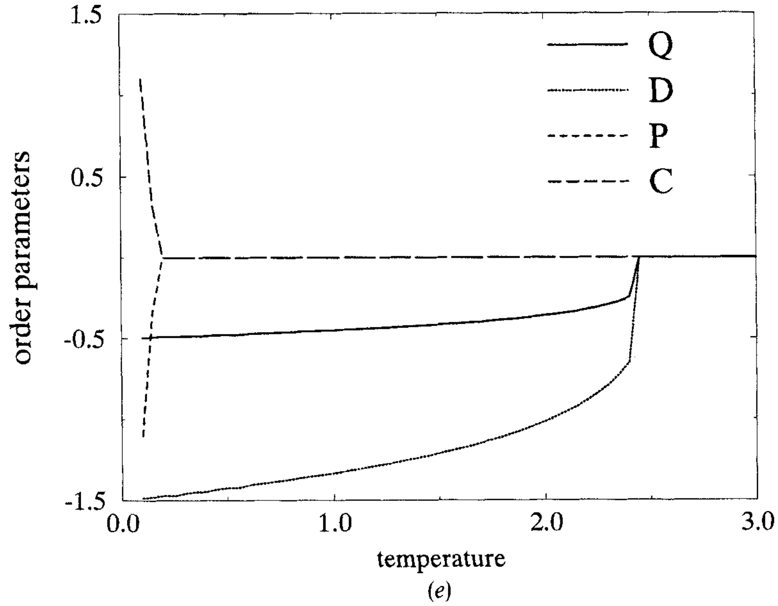

Figure 1. Orientational parameters (Q, D, P, C) as a function of temperature for a variety of biaxial coupling parameter values (*a*) $r_2 = 0{\cdot}20$, (*b*) $r_2 = 0{\cdot}30$, (*c*) $r_2 = 0{\cdot}35$, (*d*) $r_2 = 0{\cdot}50$, and (*e*) $r_2 = 0{\cdot}70$. Temperatures are normalized with respect to the Maier–Saupe transition temperature.

phase transition from the uniaxial nematic phase to the biaxial nematic phase (N_{U+}–N_B and N_{U-}–N_B) was found to be second order.

After the behaviour of pure components was studied, binary mixtures of biaxial liquid crystals were investigated. For mixtures, three parameters are needed; r_1, which reduces to a ratio of transition temperatures in the uniaxial case ($r_1=(v_1T_{NI1}/v_2T_{NI2})^{1/2}$) [22, 28], and r_2 and r_3, which measure molecular biaxiality for components 1 and 2 respectively. The equivalent biaxiality parameter for the second species is $r_3/r_1=(W_{22}/U_{22})^{1/2}$. First, a mixture of liquid crystals consisting of rod-like molecules was chosen with r_2 approximately that expected for uniaxial nematogens, ($r_1=0{\cdot}632$, $r_2=0{\cdot}163$, $r_3=0{\cdot}158$). For the rod-like uniaxial nematogen 2-fluorenyl-4′-tetradecyloxybenzoate-d_9, the temperature dependences of Q and D were experimentally measured and fit to this theory to give $r_2=0{\cdot}16\pm0{\cdot}01$ [36]. Comparison of results shown in figure 2 to an earlier study of binary mixtures of uniaxial, prolate liquid crystals ($r_1=0{\cdot}632, r_2=r_3=0$) [22] shows that the effects of increasing molecular biaxiality are to decrease the area of the N_{U+}–I coexistence region and to cause phase separation into a two component heterogeneous mixture in the biaxial phase at lower temperatures. A mixture of disk-like liquid crystal molecules ($r_1=0{\cdot}5, r_2=0{\cdot}7, r_3=1{\cdot}2$) presents qualitatively similar results as shown in figure 3. Figures 4 and 5 give the result of mixing rod-like with plate-like liquid crystal molecules. This temperature–concentration phase diagram provides evidence demonstrating that mixtures of liquid crystals comprised of prolate and oblate molecules are unstable to spinodal decomposition into two coexisting uniaxial phases, N_{U+} and N_{U-}, even when the molecules are slightly perturbed from cylindrical symmetry. A mixture of a rod-like mesogen with an

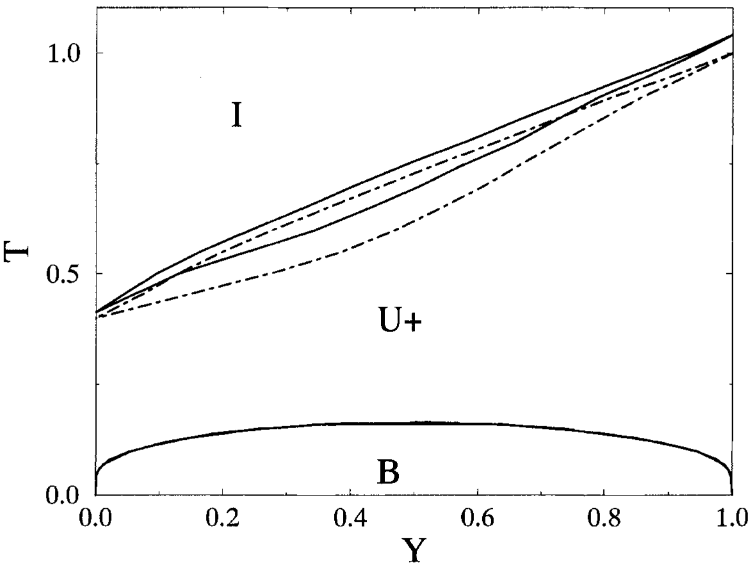

Figure 2. Temperature–concentration phase diagram for a biaxial binary mixture of rod-like liquid crystals with $r_1=0{\cdot}6325$, $r_2=0{\cdot}1633$, $r_3=0{\cdot}1581$. The two solid lines on the top of the diagram are prolate nematic (N_{U+})–isotropic (I) coexistence curves. The dotted lines are the coexistence curves if the molecules were cylindrically symmetric ($r_1=0{\cdot}6325$, $r_2=0{\cdot}0, r_3=0{\cdot}0$). Below $T=0{\cdot}17$, biaxial solutions give the minimum free energy. The bottom line is a biaxial nematic (N_B)–biaxial nematic (N_B) coexistence region. For all phase diagrams, Y is the volumetric fraction of species $i=1$ and T is the temperature normalized such that $T=1{\cdot}0$ is T_{NI} in Maier–Saupe theory.

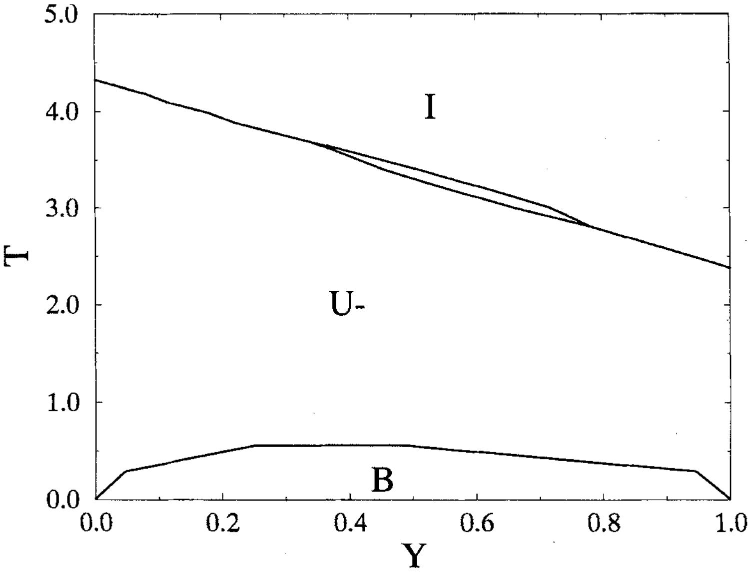

Figure 3. Temperature–concentration phase diagram for a biaxial binary mixture of disk-like liquid crystals with $r_1 = 0{\cdot}5$, $r_2 = 0{\cdot}7$, $r_3 = 1{\cdot}2$. The two solid lines on the top of the diagram are oblate uniaxial nematic (N_{U-})–isotropic (I) coexistence curves. Below $T = 0{\cdot}6$, the system is biaxial. The bottom line is a biaxial nematic (N_B)–biaxial nematic (N_B) coexistence region.

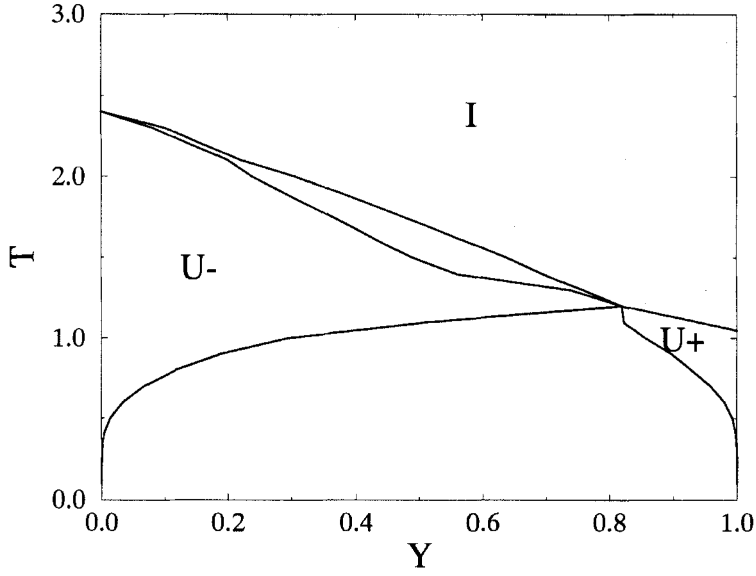

Figure 4. Temperature–concentration phase diagram for a biaxial binary mixture of disk-like liquid crystals with rod-like liquid crystals, where $r_1 = 1{\cdot}0$, $r_2 = 0{\cdot}166$, $r_3 = 0{\cdot}70$. The two solid lines on the top of the diagram are oblate nematic (N_{U-})–isotropic (I) coexistence curves. The bottom lines show that the biaxial nematic (N_B) phase is unstable, and the mixture phase separates into two coexisting uniaxial nematic phases (N_{U+} and N_{U-}).

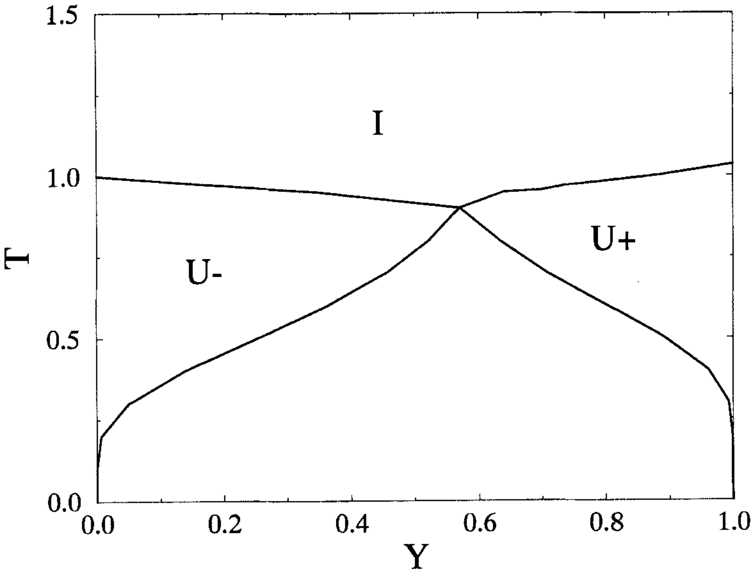

Figure 5. Temperature–concentration phase diagram for a biaxial binary mixture of disk-like liquid crystals with rod-like liquid crystals with $r_1=0{\cdot}5$, $r_2=0{\cdot}166$, $r_3=0{\cdot}50$. The bottom lines again show that the biaxial nematic (N_B) phase is unstable, and the mixture phase separates into two coexisting uniaxial nematic phases (N_{U+} and N_{U-}). Here the two pure components have roughly equal isotropic-nematic transition temperatures close to the Maier–Saupe value $T=1{\cdot}0$.

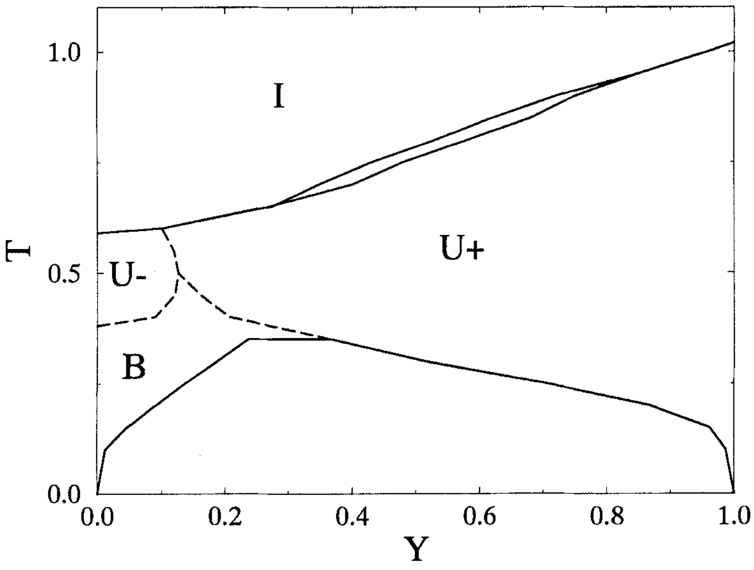

Figure 6. Temperature–concentration phase digram for a binary mixture of rod-like nematogens with highly asymmetric disk-like molecules, here $r_1=0{\cdot}6325$, $r_2=0{\cdot}166$, $r_3=0{\cdot}25$. A small region where the biaxial phase is stable exists. The dotted lines are not coexistence curves, but simply phase boundaries. The bottom line is a biaxial nematic (N_B)–uniaxial nematic (N_{U+}) coexistence region.

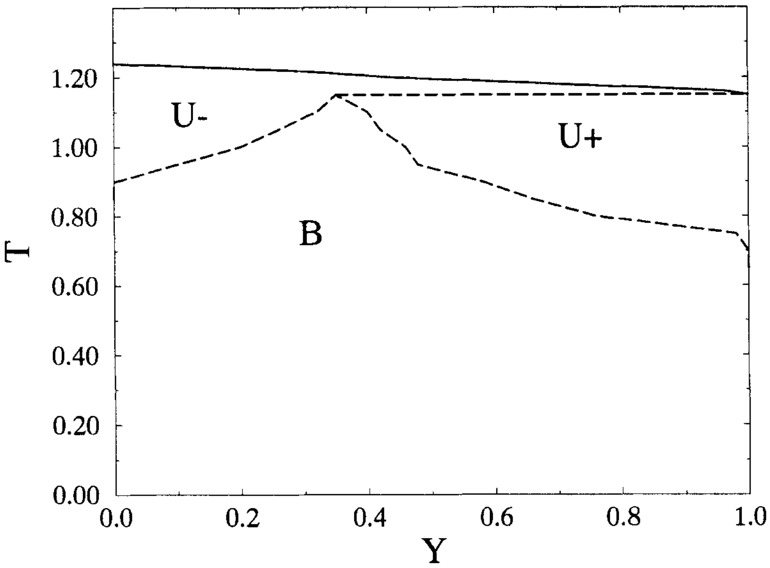

Figure 7. Temperature–concentration phase diagram for a biaxial binary mixture of flattened rod-like liquid crystals with lopsided disk-like liquid crystals, $r_1=1\cdot 0$, $r_2=0\cdot 3$, $r_3=0\cdot 35$. The dotted lines are not coexistence curves, but simply phase boundaries. For this mixture the biaxial phase is stable and is found close to the nematic–isotropic transition temperature (T_{NI}) for $Y\approx 0\cdot 33$.

asymmetrically shaped disk ($r_1=0\cdot 632, r_2=0\cdot 1633, r_3=0\cdot 25$) has a small stable biaxial phase as shown in figure 6. The last temperature–concentration phase diagram (see figure 7) shows that for mixtures of liquid crystals with asymmetric molecular shapes between those of rods and disks ($r_1=1\cdot 0, r_2=0\cdot 30, r_3=0\cdot 35$), the homogeneous mixture in the biaxial phase is stable. The parameter $r_2=0\cdot 30$ describes a flattened rod shaped molecule while $r_3=0\cdot 35$ corresponds to a lop-sided disk shaped molecule. The mixture of these two liquid crystals does not phase separate, a result which can be understood by comparing the free energy curves in figure 8. For the mixture of nearly cylindrically symmetric rods and plates in figure 8 (*a*), a concave free energy envelope shows that a heterogeneous mixture minimizes the free energy. For the mixture shown in figure 8 (*b*), the free energy curve is convex which indicates that this mixture will not phase separate but remain a homogeneous mixture. The implications of this result are discussed below.

4. Conclusions

Mean field theory of binary mixtures nematogens has been used to calculate orientational order parameters over a range of temperature and composition. Predictions of the temperature dependence of all four order parameters describing a biaxial nematic phase in a single component liquid crystal have been presented for the first time. The general result that liquid crystals with asymmetric molecules exhibit a second order phase transition when cooled from the uniaxial nematic to the biaxial nematic phase is consistent with previous predictions [2–4, 11–16]. These theoretical results motivated searches for low molecular weight biaxial nematogens [6–10, 17]. Previous experimental investigations of biaxial nematogens in uniaxial phases have been performed in which the temperature dependence of the order parameters has been

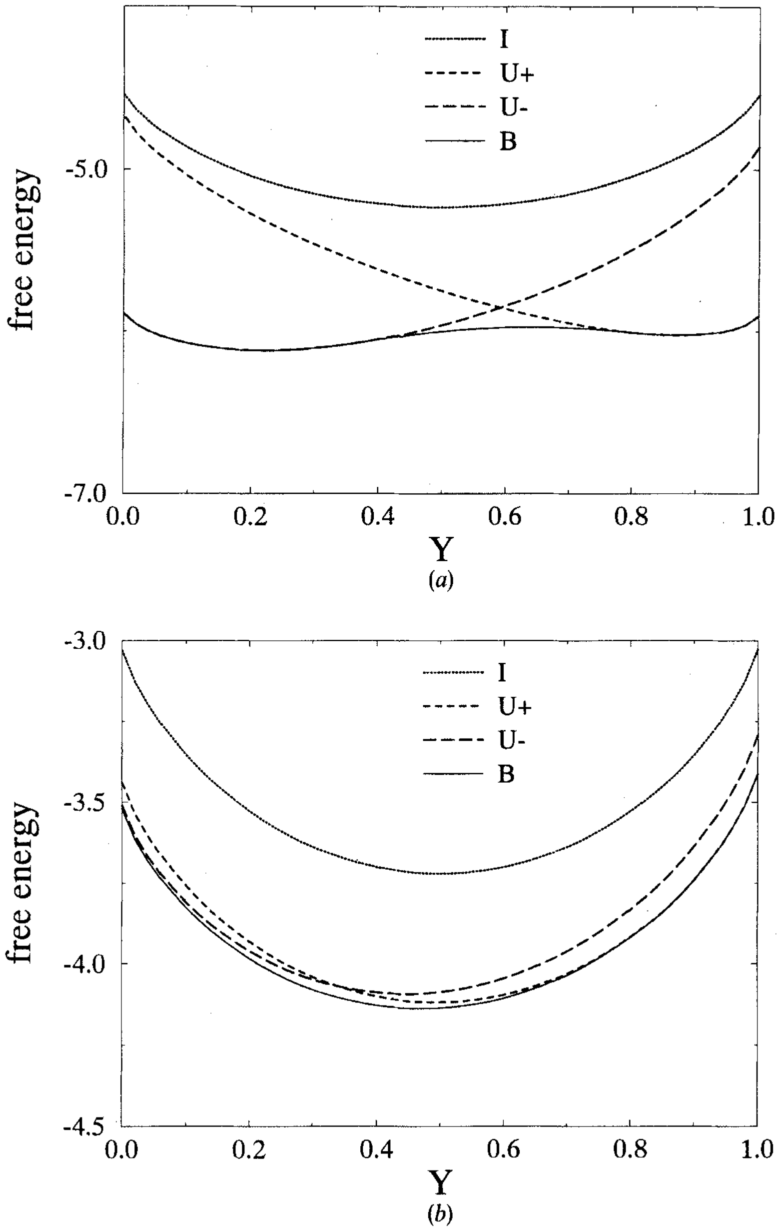

Figure 8. The free energy density at a fixed temperature is plotted at a function of concentration for the possible phases of the mixture: isotropic (I), prolate uniaxial (N_{U+}), oblate uniaxial (N_{U-}) and biaxial (N_B). For the system illustrated in figure 5 at $T=0{\cdot}50$, the free energy density of all four phases is shown in (*a*). To obtain the minimum free energy, the mixture phase separates into uniaxial components. The free energy density for the system illustrated in figure 7 at $T=0{\cdot}85$ is shown in (*b*). The minimum free energy corresponds to a homogenous biaxial phase.

successfully fitted to this model [36]. It would be interesting to perform analogous experiments on the newly reported biaxial nematic liquid crystal systems.

Behaviour of biaxial nematogens in binary mixtures is also successfully predicted using mean field theory. Previous work on nematic mixtures had suggested that it may be possible to achieve phase biaxiality by mixing rod-like nematogens and plate-like nematogens [15, 19–21]. Mean field calculations and Monte Carlo simulations of cylindrically symmetric molecules ($C_{2\infty}$ symmetry) concluded that for binary mixtures of prolate and oblate molecules, the biaxial phase is unstable to spinodal decomposition into separate inhomogeneous mixtures of uniaxial phases (N_{U+} and N_{U-}) [22–24]. In the present study it has been shown that the inclusion of slight molecular biaxiality into the theory does not affect this result. A mixture of a plate-like liquid crystal molecule and a rod-like liquid crystal molecule (with a shape anisotropy comparable to those observed in real uniaxial rod-like liquid crystal systems [36]) is predicted to phase separate into two uniaxial phases rather than to produce a stable biaxial nematic. For pure liquid crystals, systems composed of extremely asymmetric or lop-sided molecules prefer the biaxial nematic phase. However, for binary mixtures, the interesting result is that a blend of highly asymmetric molecules with opposite shape anisotropy (asymmetric rods with asymmetric disks) forms a more stable, higher temperature biaxial nematic phase than either pure component alone.

Appendix

As explained in the text, integration of the expressions needed to calculate the order parameters (equations (11) and (12)) can be performed analytically over the angular variable ϕ. This yields the following two-dimensional integrals which must be evaluated numerically.

$$Z_1 = \frac{1}{2\pi}\int_{x=0}^{1}\int_{\psi=0}^{2\pi} \exp(a) I_0(\alpha)\, dx\, d\psi, \tag{A 1}$$

$$Q_1 Z_1 + \tfrac{1}{2} = \frac{3}{4\pi}\int_{x=0}^{1}\int_{\psi=0}^{2\pi} x^2 \exp(a) I_0(\alpha)\, dx\, d\psi, \tag{A 2}$$

$$D_1 Z_1 = -\frac{3}{4\pi}\int_{x=0}^{1}\int_{\psi=0}^{2\pi} (1-x^2)\frac{b}{\alpha}\exp(a) I_1(\alpha)\, dx\, d\psi, \tag{A 3}$$

$$P_1 Z_1 = -\frac{3}{2\pi}\int_{x=0}^{1}\int_{\psi=0}^{2\pi} (1-x^2)\cos(\psi)\exp(a) I_0(\alpha)\, dx\, d\psi, \tag{A 4}$$

$$C_1 Z_1 = \frac{3}{4\pi}\int_{x=0}^{1}\int_{y=0}^{2\pi} [b\cos(\psi) + b\cos(\psi)x^2 + 2cx\sin(\psi)]\frac{I_1(\alpha)}{\alpha}\, dx\, d\psi. \tag{A 5}$$

The functions a, b, c and α are:

$$a = \tfrac{3}{2}\Lambda(\tfrac{3}{2}x^2 - \tfrac{1}{2}) - \frac{9\Lambda'}{4}(1-x^2)\cos(\psi), \tag{A 6}$$

$$b = -\tfrac{9}{4}\Lambda r_2(1-x^2) + \tfrac{9}{4}\Lambda' r_2(1+x^2)\cos(\psi), \tag{A 7}$$

$$c = -\tfrac{9}{2}\Lambda' r_2\, x\sin(\psi), \tag{A 8}$$

$$\alpha = \sqrt{(b^2 + c^2)}. \tag{A 9}$$

As a last note, the calculations are presented in the results and discussion section as functions of the volumetric fraction of molecule $i = 1$ [22, 23, 27]. Given the volume per molecule of each component, v_1 and v_2 the number density, ρ, is related to the volumetric fraction, Y, by the following simple relations.

$$Y = Y_1 = \rho_1 v_1, \tag{A 10}$$

$$(1 - Y) = Y_2 = \rho_2 v_2. \tag{A 11}$$

References

[1] Maier, W., and Saupe, A., 1958, *Z. Naturf.* (*a*), **13**, 564.
[2] Straley, J. P., 1974, *Phys. Rev.* A, **10**, 1881.
[3] Alben, R., 1973, *Phys. Rev. Lett.*, **30**, 778.
[4] Freiser, M. J., 1971, *Molec. Crystals liq. Crystals*, **14**, 165.
[5] Yu, L. J., and Saupe, A., 1980, *Phys. Rev. Lett.*, **45**, 1000.
[6] Malthête, J., Liébert, L., Levelut, A. M., and Galerne, Y., 1986, *C. r. hebd. Séanc. Acad. Sci., Paris*, **303**, 1073.
[7] Chandraskehar, S., Ratna, B. R., Sadashiva, B. K., and Raja, V. N., 1988, *Molec. Crystals liq. Crystals*, **165**, 123.
[8] Praefke, K., Kohne, B., Gündogan, B., Demus, D., Diele, S., and Pelzi, G., 1990, *Molec. Crystals liq. Crystals, Lett.*, **7**, 27.
[9] Fan, S. M., Fletcher, I. D., Gündogan, B., Heaton, N. J., Kothe, G., Luckhurst, G. R., and Praefcke, K., 1993, *Chem. Phys. Lett.*, **204**, 517.
[10] Praefcke, K., Kohne, B., Gündogan, B., Singer, D., Demus, D., Diele, S., Pelzl, G., and Bakowsky, U., 1991, *Molec. Crystals liq. Crystals*, **198**, 393.
[11] Mulder, B., and Ruijgrok, T. W., 1982, *Physica* (*a*), **113**, 145.
[12] Shih, C., and Alben, R., 1971, *J. chem. Phys.*, **57**, 3055.
[13] Caflisch, R. G., Chen, Y. G., Berker, A. N., and Dutch, J. M., 1984, *Phys. Rev.* A, **30**, 2562.
[14] Luckhurst, G. R., and Romano, S., 1980, *Molec. Phys.*, **40**, 129.
[15] Taylor, M. P., and Hertzfeld, J., 1991, *Phys. Rev.* A, **44**, 3742.
[16] Allen, M., 1990, *Liq. Crystals*, **8**, 499.
[17] Chandrasekhar, S., 1985, *Molec. Crystals liq. Crystals*, **124**, 1.
[18] Alben, R., 1973, *J. chem. Phys.*, **59**, 4299.
[19] Stroobants, A., and Lekkerkerker, H. N., 1984, *J. phys. Chem.*, **88**, 3669.
[20] Rabin, Y., McMullen, W. E., and Gelbart, W. M., 1982, *Molec. Crystals liq. Crystals*, **89**, 67.
[21] Chen, Z. Y., and Deutch, J. M., 1984, *J. chem. Phys.*, **80**, 2151.
[22] Palffy-Muhoray, P., de Bruyn, J. J., and Dunmur, D. A., 1985, *Molec. Crystals liq. Crystals*, **127**, 301.
[23] Sharma, S. R., Palffy-Muhoray, P., Bergersen, B., and Dunmur, D. A., 1985, *Phys. Rev.* A, **32**, 3752.
[24] Hashim, R., Luckhurst, G. R., and Romano, S., 1984, *Molec. Phys*, **53**, 1535.
[25] Palffy-Muhoray, P., and Hoatson, G. L., 1991, *Phys. Rev.* A, **44**, 5052.
[26] Humphries, R. L., James, P. G., and Luckhurst, G. R., 1971, *Symp. Faraday Soc.*, **5**, 107.
[27] Humphries, R. L., and Luckhurst, G. R., 1973, *Chem. Phys. Lett.*, **23**, 567.
[28] Palffy-Muhoray, P., Dunmur, D. A., Miller, W. H., and Balzarini, D. A., 1982, *Liquid Crystals and Ordered Fluids*, Vol. 4, edited by A. C. Griffin and J. F. Johnson (Plenum Press), p. 615.
[29] Luckhurst, G. R., Zannoni, C., Nordio, P. L., and Segre, U., 1975, *Molec. Phys.*, **30**, 1345.
[30] Bergersen, B., Palffy-Muhoray, P., and Dunmur, D. A., 1988, *Liq. Crystals*, **3**, 347.
[31] Goldstein, H., 1980, *Classical Mechanics* (Addison-Wesley Publishing Co.), Chap. 4, p. 147.
[32] Press, W. H., Flannery, B. P., Teukolsky, S. A., and Vetterling, W. T., 1986, *Numerical Recipes* (Cambridge University Press).
[33] Abramowitz, M., and Stegun, I. A., 1965, *Handbook of Mathematical Functions* (Dover Publications, Inc.).
[34] Wolfram, S., 1991, *Mathematica* (Addison-Wesley Publishing Co.).
[35] Kittel, C., and Kroemer, H., 1980, *Thermal Physics* (W. H. Freeman and Company).
[36] Hoatson, G. L., and Goetz, J. G., 1991, *J. chem. Phys.*, **94**, 3885.