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## Liquid Crystals

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# A perturbed hard-sphere-chain equation of state for nematic liquid crystals and their mixtures with polymers

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A perturbed hard-sphere-chain (PHSC) equation of state is presented to compute nematic–isotropic equilibria for thermotropic liquid crystals, including mixtures. The equation of state consists of an isotropic term and an anisotropic term given by the Maier–Saupe theory whose contribution disappears in the isotropic phase. The isotropic contribution is the recently presented PHSC equation of state for normal fluids and polymers which uses a reference equation of state for athermal hard-sphere chains and a perturbation theory for the square-well fluid of variable well width. The PHSC equation of state gives excellent correlations of pure-component pressure–volume–temperature data in the isotropic region and, combined with the Maier–Saupe theory, correlates the dependence of nematic–isotropic transition temperature on the pressure. Theory also predicts a nematic–isotropic biphasic region and liquid–liquid phase separation in a temperature–composition diagram of binary mixtures containing a nematic liquid crystal and a normal fluid or polymer. Theory and experiment show good agreement for pure fluids as well as for mixtures.

## 1. Introduction

Recently, mixtures of liquid crystals and polymers (i.e. polymer dispersed liquid crystals) have been attracting much attention because of their potential use as matrices for electro-optical devices [1, 2]. A distinctive phase behaviour of such mixtures is the presence of a nematic–isotropic biphasic region in a temperature–composition diagram [3, 4]. Some mixtures containing liquid crystals also exhibit liquid–liquid phase separations [5, 6] as seen in mixtures of normal fluids and polymer solutions. In conjunction with experimental works to obtain temperature–composition diagrams [3–5], several molecular–thermodynamic models have also been proposed to calculate phase diagrams of mixtures containing liquid crystals.

Brochard *et al.* [7–9], developed a conceptually simple incompressible model by combining the Flory–Huggins theory [10] for polymer solutions and blends and the Maier–Saupe theory [11–13] for nematic liquid crystals. Kyu and Chiu [14] recently extended the approach by Brochard *et al.* [7], to systems containing smectic liquid crystals using Maier–Saupe–McMillan theory [15] for smectic liquid crystals. On the other hand, Liu and Fredrickson [16] presented a rigorous incompressible-fluid theory which models molecules by worm-like chains of arbitrary stiffness and size. Incompressible-fluid models, however, neglect the effect of density on phase equilibria. To incorporate the density effect, equation-of-state theories have also been developed for pure nematic liquid crystals [17–20] and for mixtures [21–24]. Among equation-of-state theories applicable to mixtures containing nematic liquid crystals and polymers, the Flory equation of state [23] has been extensively applied to real systems, including the isotropic polymer networks immersed in nematic solvents [25].

Molecular-thermodynamic models for mixtures containing nematic liquid crystals are required to predict at least the nematic–isotropic transition of pure nematic liquid crystals. Hopefully, those models should also be able to correlate thermodynamic properties of pure liquid crystals over the nematic and isotropic regions as well as thermodynamic properties concerning the nematic–isotropic transition. At present, however, it still remains a challenging task to compute all

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thermodynamic properties associated with the nematic–isotropic transition of pure nematic liquid crystals [18–20].

In this work, we present an equation-of-state theory which correlates the pure-component properties of nematic liquid crystals very well. This theory is also applicable to nematic–isotropic and liquid–liquid equilibria for mixtures. Particular attention is given to binary mixtures of a nematic liquid crystal and a polymer. Similar to the procedure used by others [7–9], we assume that the equation of state consists of an isotropic contribution and an anisotropic contribution given by the Maier–Saupe theory [11–13] for nematic liquid crystals.

Our model, however, is different from others in the isotropic contribution. In our model, the isotropic contribution is the recently presented perturbed hard-sphere-chain (PHSC) equation of state for normal fluids and polymers [26, 27]. (The abbreviation PHSC for perturbed hard-sphere chain should not be confused with that for parallel hard spherocylinder.) For the perturbation term, the PHSC equation of state uses the second order perturbation theory of Barker and Henderson for the square-well fluid of varible width [28]. The PHSC equation of state also uses the modified Chiew equation of state [27] for athermal hard-sphere chains as the reference equation of state which represents repulsive interactions. Contrary to other equation-of-state theories for nematic liquid crystals, where repulsive interactions are often those for hard spheres or spherocylinders, repulsive interactions in our model are represented by those for hard-sphere chains. We find that, upon using the PHSC equation of state, agreement with experiment is much improved.

Equation-of-state theories have an advantage over incompressible models in that equation-of-state theories are capable of representing the pressure effect on phase behaviour. There are, however, few experimental data available regarding the effect of pressure on the phase equilibria of mixtures containing nematic liquid crystals. Therefore, for mixtures, comparison of theory with experiment is made only for systems at ambient pressure.

## 2. Pure fluids

The equation of state consists of isotropic and anisotropic contributions:

$$\left(\frac{p}{\rho k_{\mathrm{B}} T}\right)=\left(\frac{p}{\rho k_{\mathrm{B}} T}\right)_{\mathrm{iso}}+\left(\frac{p}{\rho k_{\mathrm{B}} T}\right)_{\mathrm{aniso}} \qquad (1)$$

where $p$ is the pressure, $\rho \equiv N/V$ is the number density ($N$ is the total number of molecules and $V$ is the volume), $k_{\mathrm{B}}$ is the Boltzmann constant, $T$ is the absolute temperature, and subscripts iso and aniso denote isotropic and anisotropic contributions, respectively.

### 2.1. *Isotropic contribution*

The isotropic contribution to the equation of state is the recently presented PHSC equation of state for normal fluids and polymers which uses the square-well potential of variable width [26]. The PHSC equation of state is

$$\left(\frac{p}{\rho k_{\mathrm{B}} T}\right)_{\mathrm{iso}}=\left(\frac{p}{\rho k_{\mathrm{B}} T}\right)_{\mathrm{ref}}+\left(\frac{p}{\rho k_{\mathrm{B}} T}\right)_{\mathrm{pert}} \qquad (2)$$

where subscripts ref and pert denote reference equation of state and perturbation term, respectively; these represent repulsive and attractive interactions, respectively.

The reference equation of state is the modified Chiew equation of state for athermal hard-sphere chains given by [27]

$$\left(\frac{p}{\rho k_{\mathrm{B}} T}\right)_{\mathrm{ref}}=1+\rho r^{2} b g(\sigma)-(r-1)[g(\sigma)-1] \qquad (3)$$

where $b=2\pi\sigma^{3}/3$ is the parameter that represents repulsive interactions on a segmental basis, $\sigma$ is the hard-sphere diameter, and $g(\sigma)$ is the radial distribution function at contact prior to bonding given by [27]

$$g(\sigma)=\frac{1}{1-\eta}+\frac{3}{2} \frac{\eta}{(1-\eta)^{2}}+\frac{1}{2} \frac{\eta^{2}}{(1-\eta)^{3}} \qquad (4)$$

where $\eta=r\rho\pi\sigma^{3}/6$ is the packing fraction. The last term on the right-hand side of equation (3) represents chain connectivity. For $r=1$, equation (3) reduces to the Carnahan–Starling equation of state for hard spheres [27].

The perturbation term is based on the second order perturbation theory of Barker and Henderson [26, 28] for the square-well fluid of variable well width. The square-well potential is defined by

$$u(R)=\begin{cases}\infty & R<\sigma \\ -\varepsilon & \sigma \leqslant R<\lambda\sigma \\ 0 & R \geqslant \lambda\sigma\end{cases} \qquad (5)$$

where $u(R)$ is the segment–segment pair potential, $R$ is the intersegmental distance, $\varepsilon$ is the depth of the well, and $\lambda$ is the reduced well width. The perturbation term for the equation of state is given by

$$\left(\frac{p}{\rho k_{\mathrm{B}} T}\right)_{\mathrm{pert}}=\left(\frac{p_{1}}{\rho k_{\mathrm{B}} T}\right)_{\mathrm{pert}}+\left(\frac{p_{2}}{\rho k_{\mathrm{B}} T}\right)_{\mathrm{pert}} \qquad (6)$$

where $p_1$ and $p_2$ are the first and second order perturbation terms for the equation of state given by

$$\left(\frac{p_1}{\rho k_B T}\right)_{\text{pert}} = -\frac{2}{3}\pi r^2 \sigma^3 \left(\frac{\varepsilon}{k_B T}\right) \rho \left(\Psi + \eta \frac{\partial \Psi}{\partial \eta}\right) \qquad (7)$$

$$\left(\frac{p_2}{\rho k_B T}\right)_{\text{pert}} = -\frac{1}{3}\pi r^2 \sigma^3 \left(\frac{\varepsilon}{k_B T}\right)^2 \rho \times \left[\frac{(1-\eta)^3(1-5\eta-20\eta^2-12\eta^3)}{(1+4\eta+4\eta^2)^2} \times \left(\Psi + \eta \frac{\partial \Psi}{\partial \eta}\right) + \frac{\eta(1-\eta)^4}{(1+4\eta+4\eta^2)} \times \left(2\frac{\partial \Psi}{\partial \eta} + \eta \frac{\partial^2 \Psi}{\partial \eta^2}\right)\right] \qquad (8)$$

where $\Psi$ is a function of $\eta$ and $\lambda$ resulting from the integration of the radial distribution function for hard-sphere systems over the width of the square well. The Helmholtz energy is computed from the equation of state [26].

Whereas the reference equation considers chain connectivity, the perturbation term does not. For pure fluids and mixtures considered in this work, neglect of chain connectivity in the perturbation term does not cause serious problems in performing phase equilibrium calculations.

Assuming $r = 1$ for methane, we obtained $\lambda = 1{\cdot}455$ by correlating experimental data for saturated liquid densities and vapour pressures of methane [26]. In this work, we use $\lambda = 1{\cdot}455$ for all fluids, including polymers. (In principle, an optimum reduced well width can be assigned to each fluid [26] but we do not here use that refinement.)

We have obtained a polynomial expression for $\Psi$ by fitting the analytic equation for $\Psi$ given by Chang and Sandler [29] to a polynomial function of $\eta$. $\Psi$ is given by [26]

$$\Psi(\eta) = \sum_{k=1}^{10} 3 c_k \eta^{k-1}. \qquad (9)$$

For $\lambda = 1{\cdot}455$, table 1 gives numerical coefficient $c_k$.

For a fixed reduced well width $\lambda$, the PHSC equation of state requires three parameters to describe pure fluids: number of segments per molecule $r$, hard-sphere diameter $\sigma$, and well depth $\varepsilon$.

### 2.2. *Anisotropic contribution: Maier–Saupe theory*

We use the Maier–Saupe theory [11–13] for nematic liquid crystals to calculate the anisotropic contribution to the Helmholtz energy. The anisotropic contribution to the equation of state is obtained from the anisotropic contribution to the Helmholtz energy. In the Maier–Saupe theory, the anisotropic contribution is calculated through the single-particle orientation distribution function assuming that molecules are uniaxial. In that event, the single-parent orientation distribution function depends only on $\theta$, the angle between the axis of symmetry of a molecule and the average direction of the alignment of all molecules.

Table 1. Coefficient $c_k$ for function $\Psi$ with $\lambda = 1{\cdot}455$.

| $c_k$ | Data |
|---|---|
| $c_1$ | 0·6934288007E + 00 |
| $c_2$ | 0·1031329977E + 01 |
| $c_3$ | 0·3231430915E + 00 |
| $c_4$ | − 0·7601028313E + 00 |
| $c_5$ | − 0·1898718617E + 01 |
| $c_6$ | − 0·1129836508E + 01 |
| $c_7$ | − 0·5829453430E + 00 |
| $c_8$ | − 0·4161049123E + 01 |
| $c_9$ | − 0·8040279885E + 01 |
| $c_{10}$ | 0·2470320458E + 02 |

In the Maier–Saupe theory, the order parameter specifies the degree of alignment of molecules. The order parameter is defined by

$$s \equiv \frac{3\langle \cos^2\theta \rangle - 1}{2} = \int_0^1 f(\theta)\frac{(3\cos^2\theta - 1)}{2}\,\mathrm{d}(\cos\theta) \qquad (10)$$

where $f(\theta)$ is the normalized single-particle orientation distribution function and the angular brackets denote a statistical average. Equation (10) gives $s = 0$ and $s = 1$ for random and perfectly parallel orientations, respectively.

The anisotropic contribution to the Hemlholtz energy is given by

$$\left(\frac{A}{N k_B T}\right)_{\text{aniso}} = \int_0^1 f(\theta)\ln[f(\theta)]\,\mathrm{d}(\cos\theta) - \frac{1}{2}Us^2 \qquad (11)$$

where the first and second terms on the right side represent, respectively, the decrease in entropy due to molecular alignment and anisotropic intermolecular interactions represented by dimensionless function $U$. Equation (11) assumes that the contribution from anisotropic intermolecular interactions is a quadratic function of $s$.

As a thermodynamically stable phase, the Maier–Saupe theory predicts either an isotropic phase with $s = 0$ or a nematic phase having $s$ greater than about 0·44. The Maier–Saupe theory, however, cannot describe weakly oriented systems with $s$ smaller than about 0·44 which may be present as stable phases in real systems.

As discussed in detail by Horn and Faber [30], several expressions have been proposed for function $U$ in equation (11). In this work $U$ is given by

$$U = 4r\eta^{m}\left(\frac{E}{k_{\mathrm{B}}T} + S\right) \qquad (12)$$

where exponent $m$ specifies the dependence of $U$ on the density, $E$ is a parameter which defines the energetic part of orientational interactions, and parameter $S$ crudely represents the entropic part of orientational interactions. The entropic part of orientational interactions may arise from an increase in the translational entropy in the direction of molecular alignment [30]. Parameters $E$ and $S$ are constant, independent of temperature and density.

In the original Maier–Saupe theory [11–13], $m = 2$ and $S = 0$. However, the magnitude of exponent $m$ in equation (12) has been the subject of continuing discussion [19, 30]. Exponent $m$ is often adjusted to fit experimental data for the nematic–isotropic transition [30]. The original Maier–Saupe theory also neglects the isotropic contribution to the equation of state.

Minimization of equation (11) with respect to $f(\theta)$ gives

$$f(\theta) = \frac{1}{Z}\exp\left[Us\frac{(3\cos^2\theta - 1)}{2}\right] \qquad (13)$$

where $Z$ is the single-particle orientation partition function given by

$$Z = \int_0^1 \exp\left[Us\frac{(3\cos^2\theta - 1)}{2}\right]\mathrm{d}(\cos\theta). \qquad (14)$$

Substituting equation (13) into equation (11), the anisotropic contribution to the Helmholtz energy becomes

$$\left(\frac{A}{Nk_{\mathrm{B}}T}\right)_{\mathrm{aniso}} = -\ln Z + \frac{1}{2}Us^2. \qquad (15)$$

Finally, the anisotropic contribution to the equation of state is given by

$$\left(\frac{p}{\rho k_{\mathrm{B}}T}\right)_{\mathrm{aniso}} = -\frac{1}{2}mUs^2. \qquad (16)$$

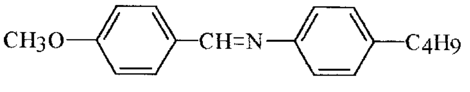
### 2.3. *Results*

In the present theory, the anisotropic contribution disappears in the isotropic phase where $s = 0$. Therefore, using equation (2), equation-of-state parameters $r$, $\sigma$, and $\varepsilon$ can be regressed from configurational thermodynamic properties in the isotropic region only. Parameters for the anisotropic contribution are then obtained from data concerning the nematic–isotropic transition using the complete equation of state which contains both isotropic and anisotropic contributions (i.e. equation (1)).

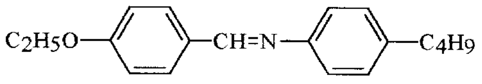
In this work, we use the data regarding the effect of pressure on the experimentally determined nematic–isotropic transition temperature ($T_{\mathrm{NI}}$) to regress parameters for the anisotropic contribution. The configurational thermodynamic properties in the nematic region are not used in the present fitting procedure. To evaluate the accuracy of the model, theoretical predictions are compared with experimental data regarding the configurational thermodynamic properties in the nematic region.

Equation-of-state parameters for normal fluids are usually regressed from experimental vapour pressures and liquid densities of saturated liquids [26] or from pressure–volume–temperature ($pVT$) data. For liquid crystals, however, saturated thermodynamic properties are not readily available at present. In the literature, only $pVT$ data are tabulated for a limited number of liquid crystals [31].

We first apply the model to pure-component $pVT$ data of *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) and *p*-ethoxybenzylidene-*p*-*n*-butylaniline (EBBA).



(MBBA)



(EBBA)

Table 2 gives PHSC equation-of-state parameters for MBBA and EBBA regressed from the $pVT$ data in the isotropic regions reported by Kuss [31]. The PHSC equation of state gives excellent correlations of pure-component $pVT$ data.

For MBBA, figure 1 (*a*) shows the effect of pressure on $T_{\mathrm{NI}}$. The nematic–isotropic transition temperature strongly depends on the pressure. Theoretical curves were calculated with several expressions for function $U$ defined by equation (12). For a pair of preset parameters $m$ and $S$, parameter $E$ was regressed from the measured $T_{\mathrm{NI}}$ at 1 bar ($10^5$ Pa). Figure 1 (*b*) shows the dependence of density change at the nematic–isotropic transition on the pressure. Theoretical curves are predictions. The density change at the nematic–isotropic transition is discontinuous; it is only about 0·2 per cent for MBBA.

The dependence of theoretical $T_{\mathrm{NI}}$ on the pressure becomes strong as the dependence of $U$ on the density rises. Theory with $m \geqslant 2$, however, overestimates the density change at the nematic–isotropic transition. Entropy parameter $S$ also affects the dependence of theoretical $T_{\mathrm{NI}}$ on the pressure. Using entropy parameter, $S = 0{\cdot}176$ with $m = 1$, gives good correlations of the

Table 2. Equation-of-state parameters for isotropic contribution.

| Substance | $T$ range/K | $r$ | $\sigma$/Å | $\varepsilon/k_B$/K | Per cent rms[a] deviation | |
|---|---|---|---|---|---|---|
| | | | | | $\rho_{liq}$ | Reference[b] |
| MBBA | 323–363 | 12·194 | 3·064 | 270·7 | 0·02 | [30] (37) |
| EBBA | 353–403 | 11·223 | 3·218 | 276·2 | 0·05 | [30] (46) |

[a] Root-mean-square relative deviations.

[b] Number in parentheses indicates number of data points used in the correlations.

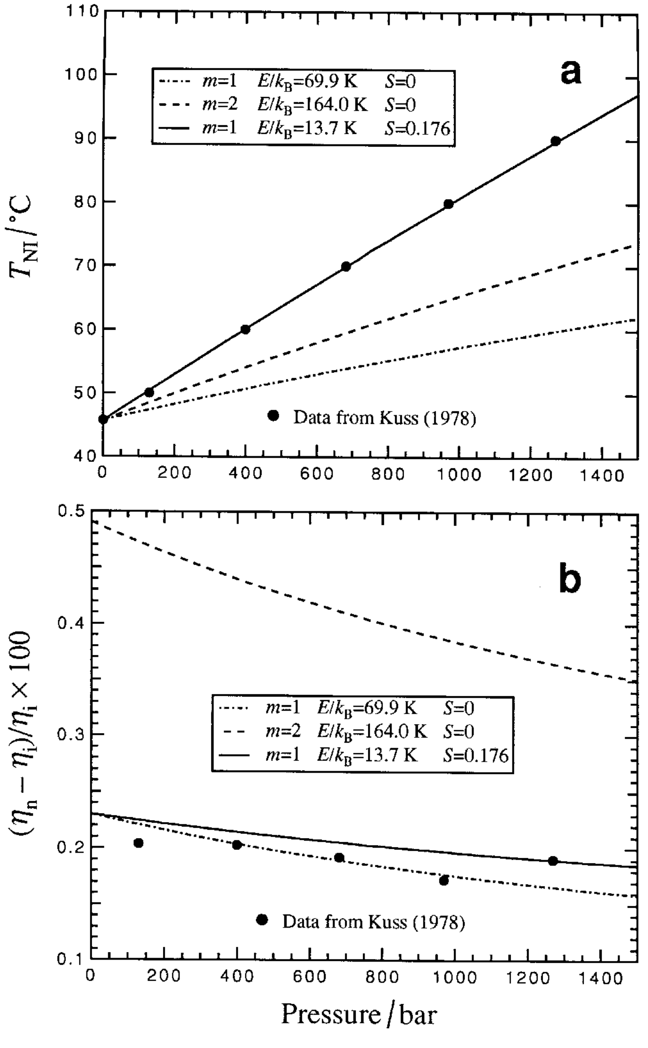


Figure 1. Pressure dependences of (*a*) nematic–isotropic transition temperature ($T_{NI}$) and (*b*) density change at the nematic–isotropic transition for MBBA. $\eta_i$ and $\eta_n$ are the packing fractions of isotropic and nematic phases, respectively, at the nematic–isotropic transition. Theoretical curves in (*b*) are predictions. Parameters shown are those for equation (12).

pressure dependence of $T_{NI}$ and the density change at the nematic–isotropic transition. Although not shown in figure 1, theory with $S=0{\cdot}176$ and $m=1$ also predicts well $pVT$ data in the nematic region. To correlate the dependence of $T_{NI}$ on the pressure, a positive entropy parameter is required. For MBBA, the entropic contribution dominates over the energetic contribution in equation (12).

Figure 2(*a*) shows the effect of pressure on $T_{NI}$ for EBBA. With $m=1$ and $S=0{\cdot}165$, theory and experiment show excellent agreement. Figure 2(*b*) shows $pVT$ data of EBBA in the nematic and isotropic regions. The $pVT$ data in the nematic region are not used in the present fitting procedure. Therefore, theoretical curves in the nematic region are predictions. Theory and experiment show good agreement over the entire nematic and isotropic regions.

The anisotropic energy $E/k_B$ for EBBA is larger than that for MBBA. This result may be closely related to the larger measured density change at the nematic–isotropic transition for EBBA [31]. The magnitude of entropy parameter $S$ is almost the same for both MBBA and EBBA.

Table 3 gives parameters for the anisotropic contribution for MBBA and EBBA.

## 3. Binary mixtures

### 3.1. *Theory*

Reference [26] also gives the isotropic contribution to the equation of state for mixtures. In the perturbation term for binary mixtures, the PHSC equation of state requires mixing rules and one adjustable parameter. The reference equation of state does not require mixing rules.

For binary mixtures, we use a one-fluid theory for the perturbation term. That theory suggests the following mixing rules to calculate the average quantities of equation-of-state parameters in equations (7) and (8):

$$\langle r^2\sigma^3\varepsilon\rangle = x_1^2 r_1^2 \sigma_1^3 \varepsilon_1 + 2x_1x_2r_1r_2\sigma_{12}^3\varepsilon_{12} + x_2^2 r_2^2 \sigma_2^3 \varepsilon_2 \tag{17}$$

and

$$\langle r^2\sigma^3\varepsilon^2\rangle = x_1^2 r_1^2 \sigma_1^3 \varepsilon_1^2 + 2x_1x_2r_1r_2\sigma_{12}^3\varepsilon_{12}^2 + x_2^2 r_2^2 \sigma_2^3 \varepsilon_2^2 \tag{18}$$

where $x_i$ is the mole fraction of component $i$ and

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2) \tag{19}$$

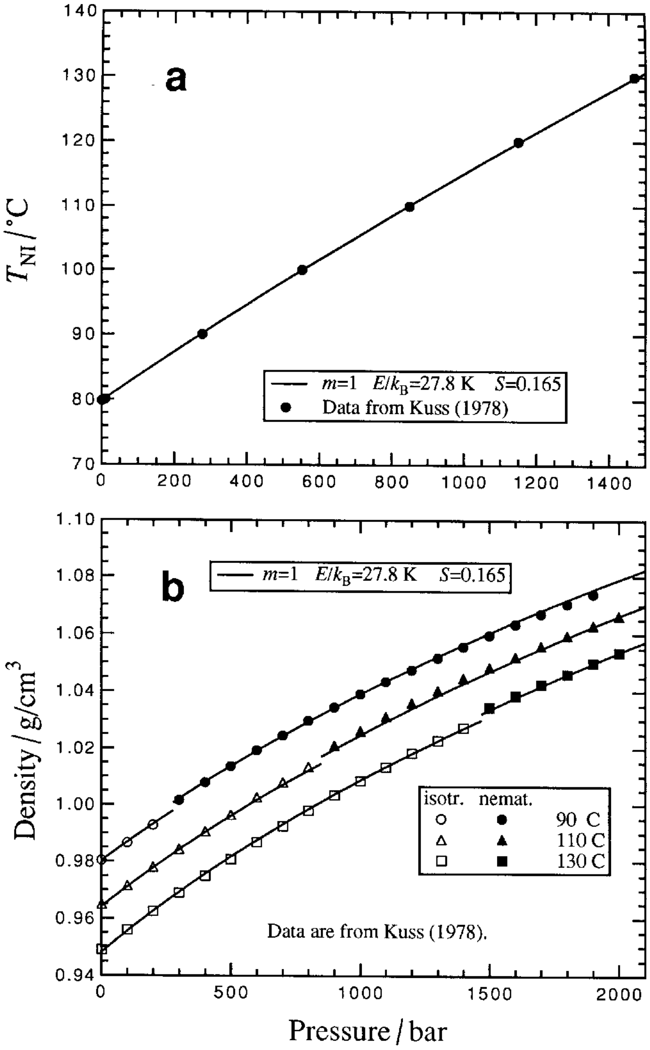


Figure 2. Pressure dependences of (*a*) nematic–isotropic transition temperature ($T_{NI}$) and (*b*) densities for EBBA. In (*b*), theoretical curves in the nematic region are predictions. Parameters shown are those for equation (12).

Table 3. Equation-of-state parameters for anisotropic contribution.

| Substance | $m$ | $E/k_B$/K | $S$ |
|---|---|---|---|
| MBBA | 1 | 13·7 | 0·176 |
| EBBA | 1 | 27·8 | 0·165 |

and

$$\varepsilon_{12} = (1 - \kappa_{12})(\varepsilon_1 \varepsilon_2)^{1/2} \tag{20}$$

where $\kappa_{12}$ is an adjustable intersegmental parameter. In equations (17) to (20) and the following equations, subscripts 1 and 2 denote properties of components 1 and 2, respectively.

For mixtures containing MBBA or EBBA, we consider the theory with $m = 1$ only. For binary mixtures of nematic liquid crystals or mixtures of a liquid crystal and a normal fluid capable of orienting in nematic solvents, we assume that the anisotropic contribution to the Helmholtz energy is given by

$$\begin{aligned}\left(\frac{A}{Nk_B T}\right)_{\text{aniso}} = {} & x_1 \int_0^1 f_1(\theta_1) \ln[f_1(\theta_1)] \, \mathrm{d}(\cos\theta_1) \\ & + x_2 \int_0^1 f_2(\theta_2) \ln[f_2(\theta_2)] \, \mathrm{d}(\cos\theta_2) \\ & - \frac{1}{2} x_1^2 U_1 s_1^2 - \frac{1}{2} x_2^2 U_2 s_2^2 - x_1 x_2 U_{12} s_1 s_2\end{aligned} \tag{21}$$

where $s_i$ is the order parameter of component $i$ defined by

$$s_i \equiv \frac{3\langle\cos^2\theta_i\rangle - 1}{2} = \int_0^1 f(\theta_i) \frac{(3\cos^2\theta_i - 1)}{2} \mathrm{d}(\cos\theta_i) \tag{22}$$

and

$$U_i = \frac{2}{3}\pi r_i^2 \sigma_i^3 \left(\frac{E_i}{k_B T} + S_i\right)\rho. \tag{23}$$

The last term on the right-hand side of equation (21) represents orientational interactions between unlike molecules. We assume that $U_{12}$ is given by

$$U_{12} = \frac{2}{3}\pi r_1 r_2 \sigma_{12}^3 \frac{E_{12}}{k_B T}\rho. \tag{24}$$

For binary mixtures, the single-particle orientation distribution functions are given by

$$f_1(\theta_1) = \frac{1}{Z_1} \exp\left[(x_1 U_1 s_1 + x_2 U_{12} s_2) \frac{(3\cos^2\theta_1 - 1)}{2}\right] \tag{25}$$

and

$$f_2(\theta_2) = \frac{1}{Z_2} \exp\left[(x_2 U_2 s_2 + x_1 U_{12} s_1) \frac{(3\cos^2\theta_2 - 1)}{2}\right] \tag{26}$$

where

$$Z_1 = \int_0^1 \exp\left[(x_1 U_1 s_1 + x_2 U_{12} s_2) \frac{(3\cos^2\theta_1 - 1)}{2}\right] \times \mathrm{d}(\cos\theta_1) \tag{27}$$

and

$$Z_2 = \int_0^1 \exp\left[(x_2 U_2 s_2 + x_1 U_{12} s_1) \frac{(3\cos^2\theta_2 - 1)}{2}\right] \times \mathrm{d}(\cos\theta_2). \tag{28}$$

By substituting equations (25) to (28) into equation (21), the anisotropic contribution to the Helmholtz energy of the mixture is also written as

$$\left(\frac{A}{Nk_{\mathrm{B}}T}\right)_{\mathrm{aniso}} = -x_1\ln Z_1 - x_2\ln Z_2 + \frac{1}{2}x_1^2U_1s_1^2 + \frac{1}{2}x_2^2U_2s_2^2 + x_1x_2U_{12}s_1s_2. \qquad (29)$$

The anisotropic contribution to the equation of state is given by

$$\left(\frac{p}{\rho k_{\mathrm{B}}T}\right)_{\mathrm{aniso}} = -\frac{1}{2}x_1^2U_1s_1^2 - \frac{1}{2}x_2^2U_2s_2^2 - x_1x_2U_{12}s_1s_2. \qquad (30)$$

Temperature–composition diagrams of mixtures are computed by equating the pressures of coexisting phases and, for each component, chemical potentials in the coexisting phases. The chemical potential of component $i$ is defined by

$$\mu_i \equiv \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j\ i} \qquad (31)$$

where $N_i$ is the number of molecules of component $i$. The Helmholtz energy of the isotropic contribution is given in [26]. Calculations were made at zero pressure, an excellent approximation for systems near atmospheric pressure.

### 3.2. *Results*

Figure 3(*a*) shows a typical theoretical temperature–composition diagram for binary mixtures containing a nematic liquid crystal and a normal fluid or polymer. The theoretical diagram shown in figure 3(*a*) is that for the mixture MBBA/*n*-hexane. Equation-of-state parameters for MBBA are given in tables 2 and 3. Equation-of-state parameters for *n*-hexane were regressed from the saturated liquid densities and vapour pressures of *n*-hexane in [26]; they are $r = 3{\cdot}220$, $\sigma = 3{\cdot}661$ Å, and $\varepsilon/k_{\mathrm{B}} = 224{\cdot}2$ K.

Theoretical curves were calculated with $\kappa_{12} = 0$ and by neglecting the orientational interactions between MBBA and *n*-hexane (i.e. $U_{12} = 0$). Mixtures of a liquid crystal and a normal fluid exhibit a nematic–isotropic biphasic region and a single-phase nematic region in a temperature–composition diagram. In addition, depending on the magnitude of isotropic interactions between unlike components as reflected by $\varepsilon_{12}$ (equation (20)), these mixtures also show liquid–liquid phase separations, as observed in mixtures of normal fluids.

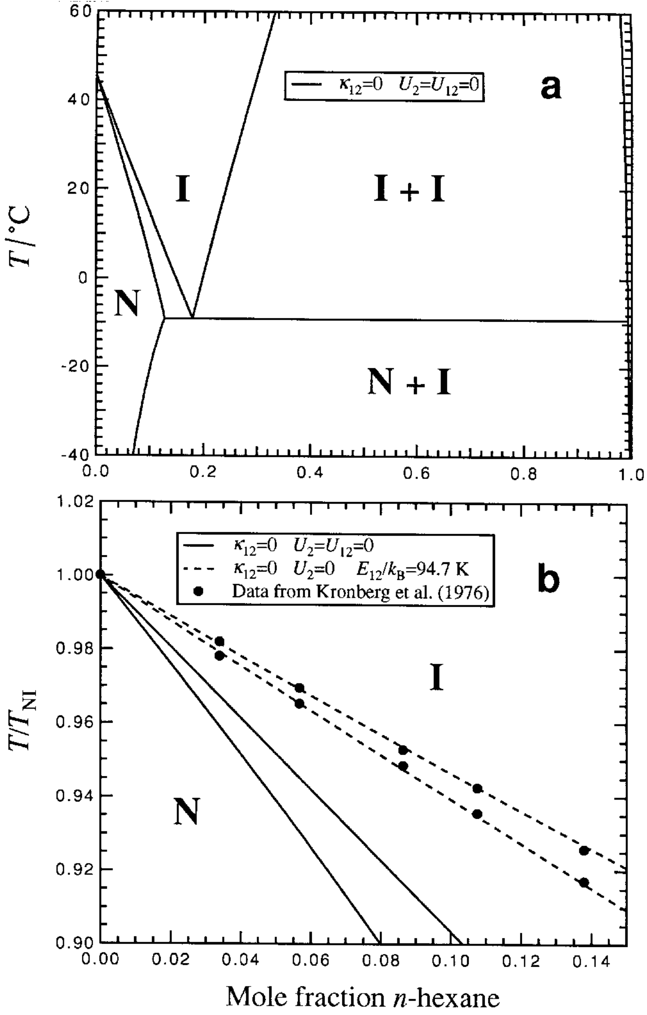


Figure 3. Temperature–composition diagram for the system MBBA/*n*-hexane; I = isotropic, N = nematic, $T_{\mathrm{NI}}$ = nematic–isotropic transition temperature for MBBA. (*a*) Shows the entire diagram and (b) shows the region near the nematic–isotropic biphasic domain of (*a*) [32].

Figure 3(*b*) compares theoretical nematic–isotropic coexistence curves with experiment for the system MBBA/*n*-hexane [32]. When the temperature and composition of a mixture lie between coexistence curves, the mixture splits into a nematic phase and an isotropic phase. In the region below the lower boundary of the biphasic region, a homogeneous nematic phase is obtained for a given set of temperature and mixture composition. Conversely, in the region above the upper boundary of the biphasic region, a homogeneous isotropic phase is stable for a given set of temperature and mixture composition.

To obtain quantitative agreement between theory and experiment in figure 3(*b*), theory needs to consider the orientational interactions between MBBA and *n*-hexane. When these orientational interactions are taken into account, *n*-hexane molecules are assumed to correlate their orientations with those of MBBA. The broken curves in figure 3(*b*) were calculated with $U_{12}$ given by equation (24) using $E_{12}$ as an adjustable binary parameter with $\kappa_{12} = 0$. Theoretical curves do not match experiment by adjusting $\kappa_{12}$ only, because that parameter affects only the isotropic contribution to the Helmholtz energy of the mixture. Parameter $\kappa_{12}$ varies the width of the nematic–isotropic biphasic region at temperatures away from $T_{\mathrm{NI}}$ of pure MBBA but does not affect the initial slope of the biphasic region near $T_{\mathrm{NI}}$ of pure MBBA. Theoretical and experimental results show excellent agreement when theory takes into account the orientational interactions between MBBA and *n*-hexane.

We now consider binary mixtures of a nematic liquid crystal and a polymer. Figure 4 compares the theoretical nematic–isotropic coexistence curves with experiment for the system EBBA/polystyrene [3]. Equation-of-state parameters for polystyrene were regressed from $pVT$ data of polystyrene in [26]; they are $r/M = 0.02123$ ($\mathrm{mol\,g^{-1}}$), $\sigma = 4{\cdot}059$ Å, and $\varepsilon/k_{\mathrm{B}} = 409{\cdot}9$ K where $M$ is the molecular weight of polymer. To obtain quantitative agreement of theory and experiment, it is necessary to consider the orientational interactions between EBBA and polystyrene.

Kronberg *et al.* [4], however, indicate that polystyrene molecules, including their oligomers, do not correlate their orientations with those of EBBA. Nuclear magnetic resonance data for deuteriated polystyrene of $M_{\mathrm{w}} = 2100\,\mathrm{g\,mol^{-1}}$ ($M_{\mathrm{w}}$ = weight-average molecular weight) also show that *para*-axes of benzene rings of deuteriated polystyrene do not orient strongly in nematic EBBA [33].

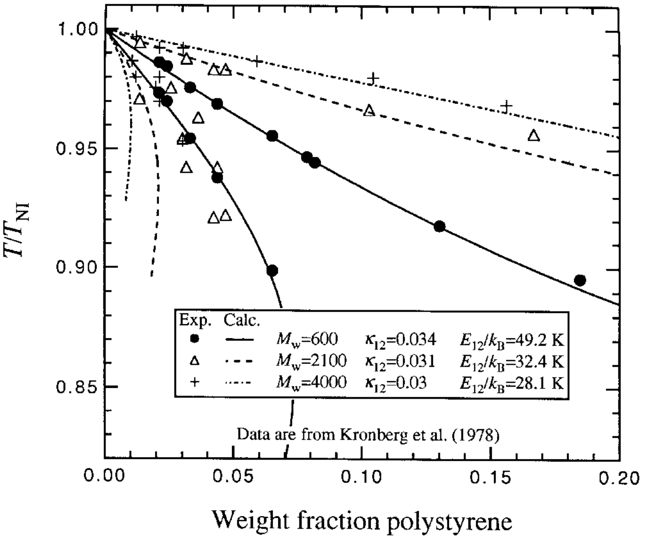


Figure 4. Nematic–isotropic coexistence curves for the system EBBA/polystyrene [3]; $T_{\mathrm{NI}}$ = nematic–isotropic transition temperature for EBBA. The anisotropic contribution to the Helmholtz energy of the mixture is given by equation (21).

Nevertheless, figure 4 compares the theoretical nematic–isotropic coexistence curves with experiment for the system EBBA/polystyrene [3] assuming that polystyrene molecules orient in nematic EBBA, regardless of the molecular weight of polystyrene. Theory and experiment show good agreement only for the system containing polystyrene of $M_{\mathrm{w}} = 600\,\mathrm{g\,mol^{-1}}$. For systems with $M_{\mathrm{w}} = 2100$ and $4000\,\mathrm{g\,mol^{-1}}$, theory does not agree with experiment for the lower boundary of the nematic–isotropic biphasic region. In these systems, theoretical curves cannot match experiment by adjusting $\kappa_{12}$ only or by introducing a composition dependence in $\kappa_{12}$. Equation (21) does not hold for the system EBBA/polystyrene when the molecular weight of polystyrene is sufficiently high.

Poor agreement of theory and experiment in figure 4 is most likely due to the incorrect anisotropic contribution to the Helmholtz energy of the mixture given by equation (21). When polystyrene molecules are present in a nematic solvent, nematic liquid crystals do not induce appreciable orientations of polymer segments but instead nematic order may be destroyed by polystyrene molecules [6]. To represent such interactions for the system EBBA/polystyrene, we propose that the anisotropic contribution to the Helmholtz energy of the mixture is given by

$$\left(\frac{A}{Nk_{\mathrm{B}}T}\right)_{\mathrm{aniso}} = x_1 \int_0^1 f_1(\theta_1)\ln[f_1(\theta_1)]\,\mathrm{d}(\cos\theta_1) - \frac{1}{2}x_1^2 U_1 s_1^2 - x_1 x_2 U_{12}^* s_1^2 \qquad (32)$$

where components 1 and 2 are EBBA and polystyrene, respectively, and the last term is proportional to $s_1^2$ representing the orientational interactions between EBBA and polystyrene. Parameter $U_{12}^*$ is assumed to be given by

$$U_{12}^* = \frac{2}{3}\pi r_1 r_2 \sigma_{12}^3 \frac{E_{12}^*}{k_{\mathrm{B}}T}\rho. \qquad (33)$$

Using equation (32) as the anisotropic contribution to the Helmholtz energy of the mixture, figures 5 (*a*) and (*b*) compare theoretical nematic–isotropic coexistence curves with experiment for the system EBBA/polystyrene. Parameter $\kappa_{12}$ is independent of polystyrene molecular weight but parameter $E_{12}^*$ is constant only for the two high molecular weight polystyrenes. In these sytems, theory with $\kappa_{12} = 0{\cdot}03$ does not predict liquid–liquid phase separations in the temperature range shown. With adjustable parameters $\kappa_{12}$ and $E_{12}^*$, theory and experiment show good agreement.

In principle, incompressible models such as that by Brochard *et al.* [7–9], can be used to correlate the phase diagrams shown in figures 3 to 5. Although we do not

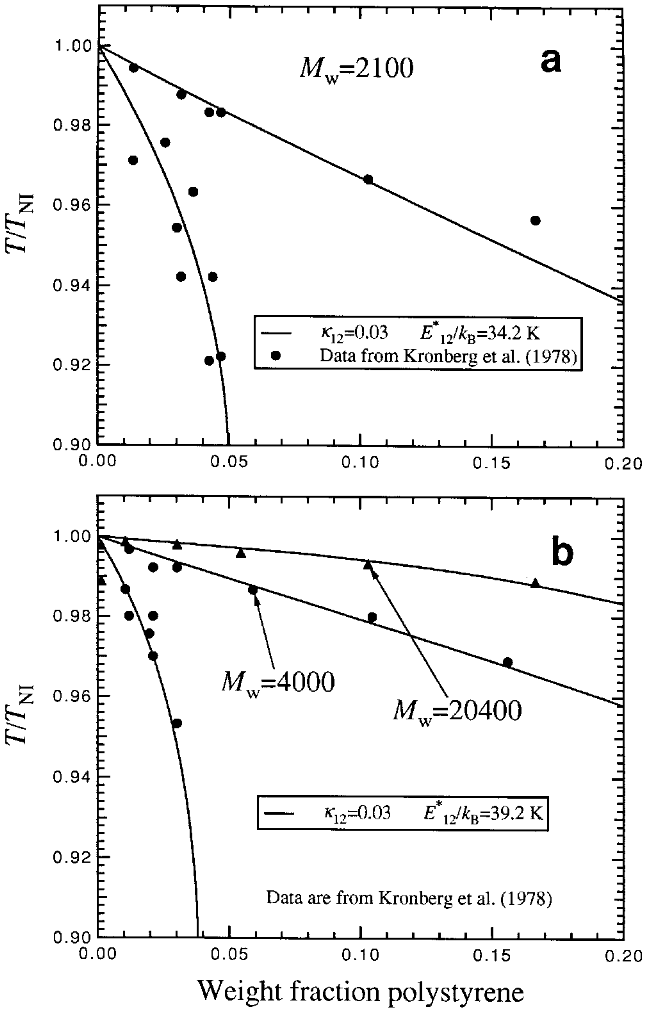


Figure 5. Nematic–isotropic coexistence curves for the system EBBA/polystyrene [3]; $T_{NI}$ = nematic–isotropic transition temperature for EBBA. The anisotropic contribution to the Helmholtz energy of the mixture is given by equation (32).

present any calculations here, the anisotropic contribution given by equation (32) can be combined with the isotropic contribution given by the incompressible Flory–Huggins theory [10]. For the system EBBA/polystyrene, such calculations may be sufficient to correlate the phase diagrams shown in figures 4 and 5.

## 4. Conclusions

A perturbed hard-sphere chain (PHSC) equation of state is presented for nematic liquid crystals and their mixtures with normal fluids and polymers. Theory uses the recently presented PHSC equation of state for normal fluids and polymers for the isotropic contribution and the Maier–Saupe theory for the anisotropic contribution. The PHSC equation of state gives excellent correlations of pure-component $pVT$ data for MBBA and EBBA over the isotropic and nematic regions. Theory also correlates the dependence of nematic–isotropic transition temperature on the pressure for EBBA and MBBA.

The PHSC equation of state predicts a nematic–isotropic biphasic region in a temperature–composition diagram of binary mixtures containing a liquid crystal and a normal fluid or polymer. For the system MBBA/*n*-hexane, the theoretical nematic–isotropic biphasic region show good agreement with experiment when *n*-hexane is considered capable of orienting in nematic MBBA. For the system EBBA/polystyrene, where polystyrene molecules do not correlate their orientations with those of EBBA, a new expression is proposed for the anisotropic contribution to the Helmholtz energy of the mixture given by equation (32). Using equation (32) as the anisotropic contribution, theory and experiment show quantitative agreement for the system EBBA/polystyrene.

Despite simplifying assumptions in the Maier–Saupe theory to take into account the anisotropic contribution, agreement between theory and experiment is encouraging for pure fluids as well as for mixtures, probably because the present model uses an equation of state for the isotropic contribution which is better than those used previously.

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