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Phenomenological description of the crystal–liquid crystal phase diagram

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A new Landau-type phenomenological free energy function to describe the phase diagram of uniaxial anisotropic materials is proposed. The resulting phase diagram includes crystalline, smectic A, nematic and isotropic states, as well as a theoretically possible plastic solid state. Depending on the parameters of the free energy, smectic A phase may or may not be present for a given material. The obtained topologies of the temperature–pressure phase diagram qualitatively agree with results from computer simulations of model liquid crystalline materials.

1. Introduction

The description of phase behaviour of anisotropic organic materials remains one of the most challenging problems in today's soft condensed matter physics. Because of the large number of degrees of freedom involved (translational, orientational, conformational), the direct realistic computer modelling of such materials becomes prohibitively expensive. Although in recent years, several simulations of real liquid crystalline materials have been performed [1–7], they usually calculated materials properties in a specific phase or in some narrow temperature interval, but not a complete phase diagram. It becomes important, therefore to develop simplified models, as well as purely theoretical approaches, to study phase behaviour in such materials.

Computer simulations on model anisotropic fluids (like hard ellipsoid, hard rod, hard spherocylinder or Gay–Berne) are often used to obtain new knowledge of the topology of the crystal–liquid crystal phase diagram. In their studies of a Gay–Berne [8] system (consisting of ellipsoidal rigid particles interacting via orientation-dependent Lennard–Jones potential), Luckhurst *et al.* [9], and de Miguel *et al.* [10–13] investigated the role of shape and energy anisotropies in determining temperature–density and temperature–pressure phase diagrams. Depending on the pressure and shape and/or energy anisotropy, a Gay–Berne system can have one of the following phase sequences on cooling from isotropic liquid:

I–N–SmA–Cr

I–SmA–Cr

I–N–Cr

I–Cr

where I = isotropic liquid, N = nematic, SmA = smectic A, Cr = crystal. Most of these transitions are first order, with the possible exception of the N–SmA transition, which is usually second order (or very weakly first order). Because of the large number of phases and different possible phase sequences, it remains a strong challenge to describe such a phase diagram theoretically.

Phenomenological theories of phase transitions in liquid crystals started from the classical works of Onsager [14] and Maier and Saupe [15] describing the nematic–isotropic (N–I) transition. De Gennes [16] and McMillan [17] developed phenomenological models for the isotropic–nematic–smectic A phase diagram, and Chen and Lubensky [18] proposed a theory for the nematic–smectic A–smectic C phase diagram. However, there is no unified theory that includes all liquid crystalline, isotropic and crystalline phases.

The other theoretical approach includes molecular theories, like scaled-particle theory (SPT) or density functional theory (DFT). The SPT approach was used by Gelbart and Barboy [19] to study the N–I transition; it was not applied to other transitions. The DFT, on the other hand, has been used extensively for many liquid crystalline systems in recent years. This method, originally developed by Ramakrishnan and Yussouf [20] to describe crystal melting, has been successfully applied to describe, with very high accuracy, liquid crystalline phase diagrams of several model fluids [21–26]. Our recent results in applying DFT to Gay–Berne fluid [26] suggest that it is possible to describe correctly all the complex topology of realistic liquid crystal systems. However, even the DFT calculation of the phase diagram for a model liquid crystal requires significant computing effort (although it is considerably less than Monte Carlo or molecular dynamics simulations), and it is desirable to

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have a simple Landau-type theory that would combine all types of phases in one phase diagram. Such a theory is proposed in this paper.

The proposed approach, for the first time, combines the isotropic, nematic, smectic A and crystal phases in a single, simple free energy expression with two coupled scalar order parameters. Depending on the value of a coupling parameter between orientational and translational degrees of freedom, it is possible to obtain phase diagrams either with or without smectic A phase. For different pressures different phase sequences exist, and the topology of the phase diagram compares qualitatively well with the results of computer simulations by Brown *et al.* [13].

The paper is organized as follows: in § 2 we describe the free energy function and the meaning of the order parameters; in § 3 phase diagrams are presented for several specific cases, and classification of the phase diagram topologies is made; finally, in § 4 we discuss our results and the possible extensions of the theory.

2. Free energy function

Let us consider a fluid consisting of uniaxial anisotropic particles. If the anisotropy is strong enough, at low temperatures and/or high densities, particles would prefer to align parallel to one common axis. It is possible then to introduce the orientational order parameter S as the second Legendre polynomial of the cosine of the angle between this common axis and the long axis of a given particle, averaged over all the particles in the system:

$$S=\frac{3\langle\cos^2(\mathbf{n},\mathbf{z})\rangle-1}{2}. \tag{1}$$

Following Maier and Saupe [15], one can write the orientational part of free energy as a fourth-order polynomial in S. The zero-order term is irrelevant since it amounts only to the change of the zero energy level; the first-order term is always zero because $S=0$ corresponds to the equilibrium isotropic phase, hence the orientational part of the free energy can be written as:

$$F=\frac{1}{2}AS^2-\frac{1}{3}BS^3+\frac{1}{4}DS^4 \tag{2}$$

where A is a variable determining the phase transition, and B and D are constants. We consider the case of prolate uniaxial particles, so in the nematic $S>0$, and thus B should be positive. The case of $B<0$ will not be considered in this study.

To introduce a smectic (positional) order parameter, one assumes that the mass density of the liquid crystal is non-uniform along the z-axis:

$$\rho(z)=\rho_0+\delta\rho\,\mathrm{Re}\{\exp(\mathrm{i}qz)\}$$

and uses a new order parameter $m=(\delta\rho/\rho_0)$. The value of the wavenumber q does not enter into the McMillan [17] theory describing smectic ordering—it must be determined on the basis of specific molecular considerations. In an isotropic phase, $S=0$ and $m=0$; in the nematic, S is non-zero and $m=0$; in the smectic, both S and m are non-zero.

In order to include the crystalline phase in the framework of the McMillan theory, we must modify the definition of the positional order parameter to account for the possibility of three-dimensional as well as one-dimensional ordering. Let us first assume that the mass density of the system is described by:

$$\rho(\mathbf{r})=\rho_0+\delta\rho\sum_l \mathrm{Re}\{\exp(\mathbf{i}\mathbf{q}_l\mathbf{r})\}$$

where q_l are reciprocal lattice vectors corresponding to the 'best' crystal structure (more details about the selection of such structure can be found, e.g. in [27]). It is important to note that, in principle, for every crystal structure there is a separate Landau free energy expansion in powers of $\delta\rho$. However, we assume that the crystal structure does not change within the investigated temperature region, so that one Landau expansion can be used.

The formula for the mass density can be also applied to describe smectic A phase if we set $\mathbf{q}_1=(0,0,q)$, $\mathbf{q}_2=-\mathbf{q}_1$. Again, the Landau expansion in powers of $\delta\rho$ for this structure would be different from the crystal one.

Let us now introduce a positional order parameter m defined as follows:

$$m=(\delta\rho/\rho_0)(1-2\delta_{Q_x^2 0}\delta_{Q_y^2 0})$$

where we define $Q_x^2=\Sigma_l\, q_{lx}^2$, $Q_y^2=\Sigma_l\, q_{ly}^2$ and δ is the usual Kronecker symbol. The meaning of this definition is to separate the 'smectic' and 'crystal' parts of the Landau free energy into two separate branches—positive order parameter for crystal phase, negative order parameter for smectic phase. Both N–A and Cr–N transitions would be the order–disorder transitions, while the Cr–SmA transition would be simply a switching between the two ordered states. Further, we postulate that the free energy is a smooth function of m which, within the investigated interval of temperatures, can be expanded in Taylor series up to the fourth order.

Because of the difference between positive and negative m, the Landau free energy expansion in m must include the cubic term pm^3, absent in McMillan theory. In the complete thermodynamic analysis of the system, p must be considered another independent variable, and the full phase diagram must be calculated. While this is an easy thing to do, such a phase diagram is not of much interest for real systems because p is not an independent variable, but a function of temperature. At low temperatures, the cubic term is negative, favouring crystal ordering; at high temperatures, it is positive, favouring smectic ordering. It must change sign at some temperature to represent the (first order) crystal–smectic transition. Thus, after redefining positional order parameter and introducing the new (cubic) term, we can write the positional part of the free energy as:

$$F_{\mathrm{tr}} = \frac{1}{2} r m^2 - \frac{1}{3} p m^3 + \frac{1}{4} u m^4 \qquad (3)$$

where r is a variable measuring distance to the transition, u is a positive constant, and p is temperature-dependent. When p is positive, a 'favoured ordered phase' is crystal; otherwise, it is smectic. To describe the crystal–smectic transition, we postulate the following dependence of p on r:

$$p = r_0 - r \qquad (4)$$

here $r_0 > 0$ is a 'latent temperature of crystal–smectic transition'. Note, however, that this 'transition' is purely hypothetical, since at $r = r_0$, the homogeneous phase is the lowest energy phase; neither smectic nor crystal are even stable. Only when the coupling between orientational and translational degrees of freedom is taken into account, does the 'virtual' crystal–smectic transition become a true transition.

The assumption that both crystal and smectic phases can be described by one Landau free energy is certainly non-universal and will not apply to all liquid crystal materials. For it to be valid, the smectic phase (if it exists) should be rather narrow. Thus, this theory should be applicable primarily to particles with a relatively weak shape anisotropy, where smectic phase is induced by van der Waals attractive forces. At this stage, when parameters of the model are purely phenomenological, it is still difficult to quantify this criterion. The more general Landau-type theory of crystal–liquid crystal transitions should have separate order parameters for smectic and transverse ordering, and reduce to the form proposed here only in the limit of a narrow smectic phase.

The coupling between orientational and translational degrees of freedom was first proposed by McMillan. In his model, this coupling is proportional to m^2 multiplied by some function of S. Let us write this term as:

$$F_{\mathrm{c}} = -\frac{1}{2} C m^2 S^2 (1 - \lambda S) \qquad (5)$$

where C and λ are non-negative constants.

The total free energy of the system can be written as:

$$F = \frac{1}{2} A S^2 - \frac{1}{3} B S^3 + \frac{1}{4} D S^4 + \frac{1}{2} r m^2 - \frac{1}{3}(r_0 - r) m^3 + \frac{1}{4} u m^4 - \frac{1}{2} C m^2 S^2 (1 - \lambda S). \qquad (6)$$

In the next section, we analyse phase behaviour of the free energy, from equation (6), in the A–r plane and in the T–P (temperature–pressure) plane. The role of the coupling constant C, the adjustment parameter λ, and the 'latent crystal–smectic transition temperature' r_0 in determining phase diagrams is elucidated and three major classes of liquid crystalline materials (e-class, g-class and r-class) with different topologies of the T–P phase diagram are described.

3. Phase diagrams

3.1. *Equilibrium states and free energy minima*

Minimization of the free energy expression (6) yields the following two equations for the equilibrium values of order parameters S, m:

$$\begin{aligned} &(A - Cm^2)S - \left(B - \frac{3}{2}\lambda C m^2\right) S^2 + D S^3 = 0 \\ &[r - CS^2(1 - \lambda S)]m - (r_0 - r)m^2 + u m^3 = 0. \end{aligned} \qquad (7)$$

There are four sets of solutions of these equations, corresponding to four possible phases:

(1) Isotropic liquid: $m = 0$, $s = 0$.

(2) Nematic liquid crystal:

$$m = 0,\ S = \frac{B + (B^2 - 4AD)^{1/2}}{2D}.$$

(3) Plastic solid:

$$S = 0,\ m = \frac{r_0 - r + (r_0 - r)^2 - 4ur^{1/2}}{2u}.$$

(4) Crystal or smectic A:

$$S = \frac{\left(B - \frac{3}{2} C \lambda m^2\right) + \left[\left(B - \frac{3}{2} C \lambda m^2\right)^2 - 4(A - Cm^2)D\right]^{1/2}}{2D}$$

$$m = \frac{r_0 - r \pm \{(r_0 - r)^2 - 4u[r - CS^2(1 - \lambda S)]\}^{1/2}}{2u},$$

where the plus sign corresponds to the crystal case when $r < r_0$, and the minus sign corresponds to the smectic case when $r > r_0$. Note that in this last set, m and S are coupled in the solution, and it is very difficult to produce an exact analytical expression—instead, one has to resolve to numerical methods to determine phase boundaries.

3.2. *Phase diagram in the A–r plane*

We consider a system with the following values of parameters: $B=1.0$, $D=2.0$, $r_0=0.1$, $\lambda=1.0$, and calculate phase diagrams for three different values of the coupling constant C: 0, 1.0, and 1.5. As will be seen, change in the coupling constant leads to change in the topology of the phase diagram.

In figure 1 (*a*), the phase diagram is plotted in the A–r plane for $C=0$. There are four phases: isotropic liquid, plastic solid, nematic, and crystal. For this system, there are only two possible phase sequences:

I–Cr or I–N–Cr

(we assume that plastic solid phase occurs for non-physical conditions, e.g. negative pressures).

In figure 1 (*b*), the same phase diagram is shown for $C=1.0$. Now, there is an island of smectic A phase,

(*a*)

(*b*)

Figure 1. Phase diagram in the A–r plane for the cases $C=0$, $\lambda=1.0$, $r_0=0.1$ (*a*), $C=1.0$, $\lambda=1.0$, $r_0=0.1$ (*b*), and $C=1.5$, $\lambda=1.0$, $r_0=0.1$ (*c*). Phases: I = isotropic, N = nematic, P = plastic solid, SmA = smectic A, Cr = crystal.

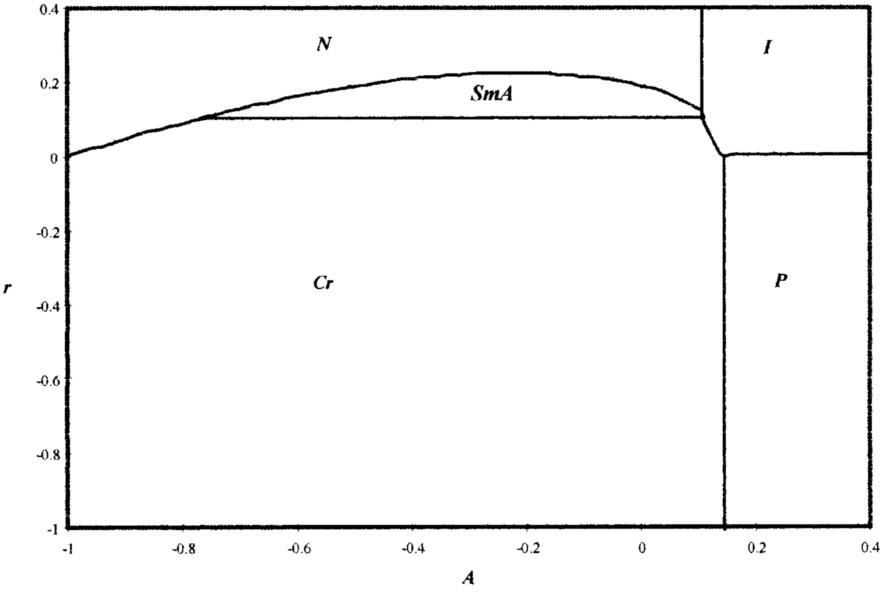


Figure 1. (*continued*). (*c*)

sandwiched between crystal and nematic. The coupling also moved the crystal–nematic line toward higher r, so the crystal–isotropic transition becomes a segment, rather than a point, as in the previous case. For this topology, depending on a selected trajectory, the system can go through any of the following phase sequences:

I–Cr I–N–Cr I–N–SmA–Cr

Finally, in figure 1 (*c*), the case of strong coupling ($C=1.5$) is shown. The smectic A region has grown so large that it now coexists with the isotropic state, although in a very narrow region.

To understand better the role of all parameters of the free energy and to classify liquid crystals by the topology of their phase diagram, we will next consider the temperature–pressure (T–P) phase space.

3.3. *Temperature–pressure phase diagrams*

The possible T–P phase diagrams were qualitatively analysed by Brown *et al.* [12, 13] in their studies of Gay–Berne fluid. If we neglect the exotic cases of reentrant phases, one can see that all phase diagrams fall into three classes (assuming there are no tilted or hexatic phases):

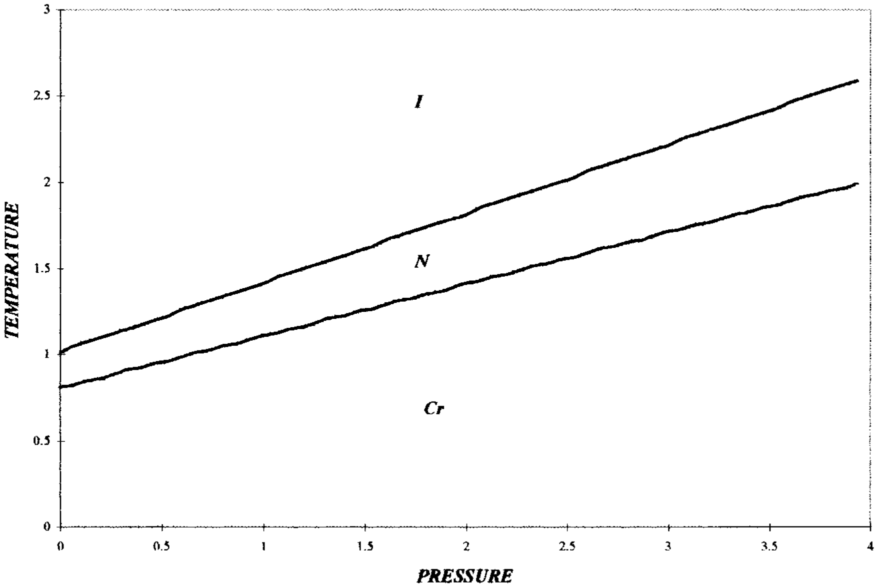
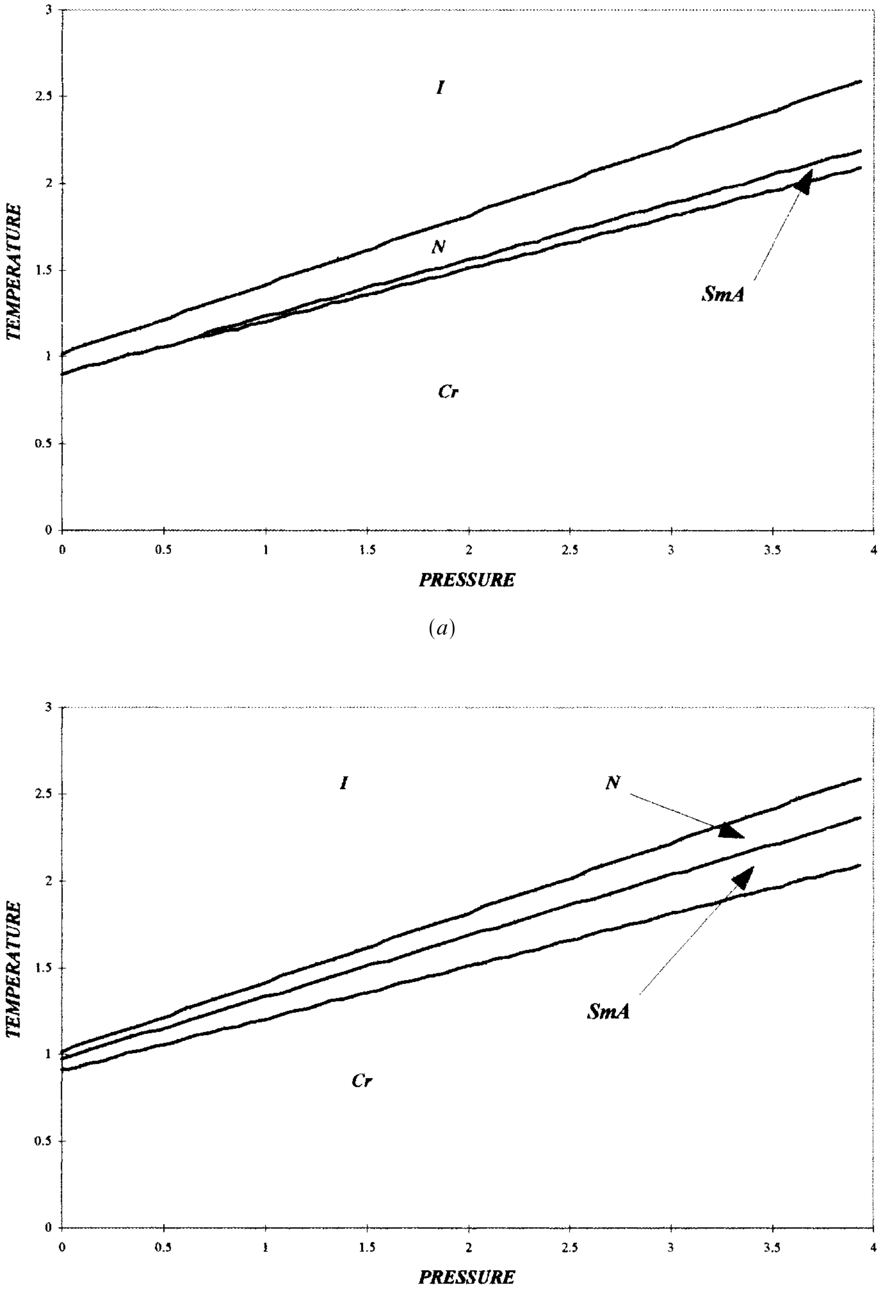


Figure 2. Temperature – pressure phase diagram for the E-class system: $T_1=0.9$, $T_2=0.8$, $\alpha_1=0.4$, $\alpha_2=0.3$, $C=0.0$, $\lambda=1.0$, $r_0=0.1$. Phases: I = isotropic, N = nematic, SmA = smectic A, Cr = crystal.



(*a*)

(*b*)

Figure 3. Temperature – pressure phase diagram for R-class systems: $T_1=0.9$, $T_2=0.8$, $\alpha_1=0.4$, $\alpha_2=0.3$, $C=0.4$, $\lambda=0.0$, $r_0=0.1$ (*a*); $T_1=0.9$, $T_2=0.8$, $\alpha_1=0.4$, $\alpha_2=0.3$, $C=1.0$, $\lambda=0.0$, $r_0=0.1$ (*b*); $T_1=0.9$, $T_2=0.8$, $\alpha_1=0.4$, $\alpha_2=0.3$, $C=1.7$, $\lambda=0.0$, $r_0=0.1$ (*c*). Phases: I = isotropic, N = nematic, SmA = smectic A, Cr = crystal.

(1) E-class (E = ellipsoid)—liquid crystals that do not form smectic phases under any conditions. A schematic *T–P* phase diagram is shown for such a system in figure 12 of [12] (in this figure, crystal phase is labeled SmB—for more discussion of this topic see [13]). It has only crystal and isotropic phases at low temperatures and isotropic, nematic and crystal at high temperatures. The E-class particles have ellipsoidal (or close to ellipsoidal) shape and a weakly anisotropic attractive or repulsive potential. Since ellipsoids do not form smectic phases, and attractive interaction is not sufficiently anisotropic, smectics are not observed at any temperature or pressure.

(2) G-class (G = Gay–Berne)—liquid crystals that can form smectic phases in a finite region of temperature and pressure. Such systems were simulated by Brown *et al.* [13] in their studies of Gay–Berne fluids with shape anisotropies $3 \leqslant \kappa \leqslant 4$ and energy anisotropy 5. Although the

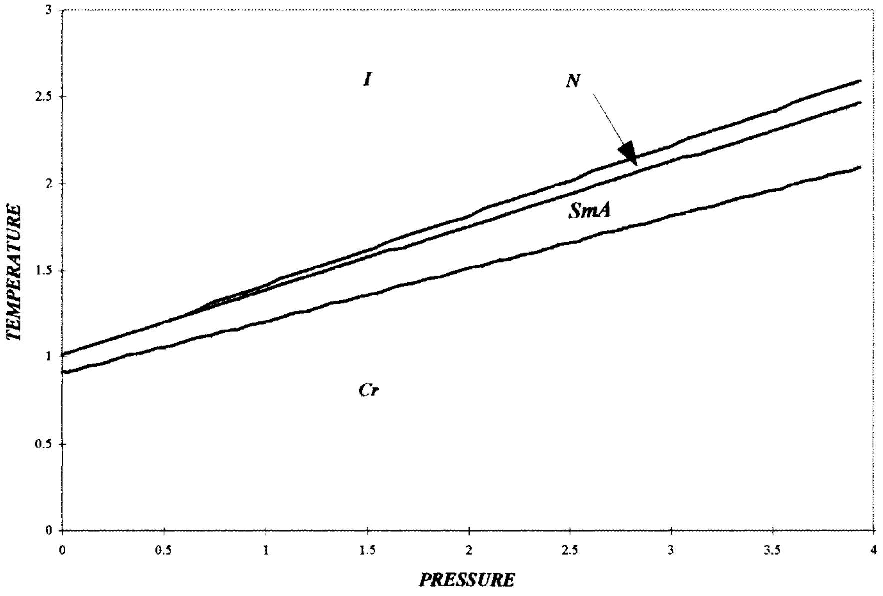


Figure 3. (*continued*). (*c*)

particles have ellipsoidal shape, the anisotropy of attractive interaction is so strong that is allows the formation of smectic A phase for some intermediate pressures and temperatures. Smectic A phase then forms an island in a phase plane that is squeezed out at both high and low temperatures.

(3) R-class (R = rods)—liquid crystals that can form smectic phases at any temperature given the right pressure. Such particles have rodlike or spherocylindrical shape and would form smectic phase even without attractive potential (lyotropic smectics). The addition of the interparticle potential makes the system thermotropic, but the topology of the phase diagram is not changed significantly compared with the lyotropic system: at any temperature, the increase in pressure corresponds to the I–N–SmA–Cr sequence.

In our model, the class of the phase diagram is determined by the three parameters C, λ and r_0:

(1) If $C(1-\lambda) > r_0$, the system is of R-class.
(2) If $C(1-\lambda) < r_0$, and $\max[CS^2(1-\lambda S)] > r_0$, the system is of G-class.
(3) If $\max[CS^2(1-\lambda S)] < r_0$, the system is of E-class.

Below, we illustrate all three classes assuming linear dependence of both A and r on temperature and pressure:

$$A = T - T_1 - \alpha_1 P$$

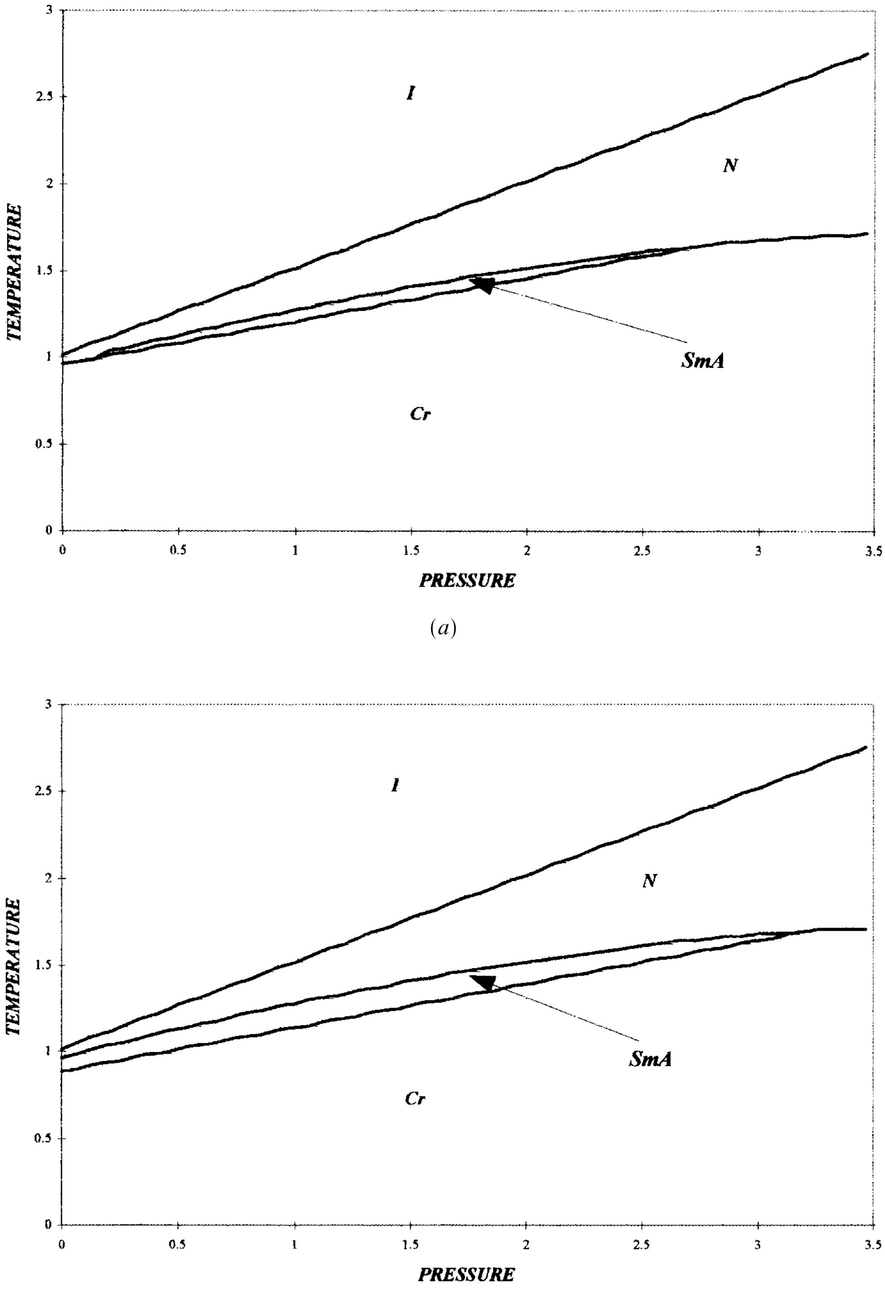
$$r = T - T_2 - \alpha_2 P.$$

Units of pressure and temperature are arbitrary; we assume that the temperature and density region is 'small' so that linear dependence of phase transition temperatures on pressure is justified. To compare these results with an actual temperature–pressure phase diagram, it would be necessary to establish a more precise physical meaning of the parameters in the free energy (6). Instead, we simply determine possible topologies of phase diagrams in the T–P plane.

In figure 2, the phase diagram is shown for the case $T_1 = 0.9$, $T_2 = 0.8$, $\alpha_1 = 0.4$, $\alpha_2 = 0.3$, $C = 0$, $\lambda = 1.0$, $r_0 = 0.1$ (E-class). Since the McMillan coupling constant is zero, no smectic phase exists at any pressure. The nematic phase separates the crystal and the isotropic phases and becomes increasingly more stable as pressure grows. Both crystal–nematic (Cr–N) and nematic–isotropic (N–I) transitions are strongly first order.

In figure 3, phase diagrams are shown for the R-class. At zero (atmospheric) pressure, it is possible to observe a full sequence I–N–SmA–Cr (*b*), a sequence I–N–Cr (*a*), or a sequence I–A–Cr (*c*). The three cases vary only in the value of the McMillan coupling constant C: $C = 0.4$ (*a*), 1.0 (*b*), and 1.7 (*c*). Other parameters are: $T_1 = 0.9$, $T_2 = 0.8$, $\alpha_1 = 0.4$, $\alpha_2 = 0.3$, $\lambda = 0.0$, $r_0 = 0.1$. At high pressures, all three cases show the same behaviour, exhibiting all four phases; as pressure increases, smectic and nematic regions both become broader. The Cr–N, Cr–SmA and N–I transitions are relatively strongly first-order; the N–A transition is weakly first order, in qualitative agreement with experimental observations.

In figure 4 similar scenarios are shown for the G-class. Again, it is possible to achieve any phase sequence at atmospheric pressure: the I–N–Cr sequence (*a*) is obtained for the set $T_1 = 0.9$, $T_2 = 0.8$, $\alpha_1 = 0.5$, $\alpha_2 = 0.25$,



(*a*)

(*b*)

Figure 4. Temperature – pressure phase diagram for G-class systems: $T_1 = 0.9$, $T_2 = 0.8$, $\alpha_1 = 0.5$, $\alpha_2 = 0.25$, $C = 1.5$, $\lambda = 1.0$, $r_0 = 0.15$ (*a*); $T_1 = 0.9$, $T_2 = 0.8$, $\alpha_1 = 0.5$, $\alpha_2 = 0.25$, $C = 1.5$, $\lambda = 1.0$, $r_0 = 0.08$ (*b*); $T_1 = 0.9$, $T_2 = 0.825$, $\alpha_1 = 0.5$, $\alpha_2 = 0.25$, $C = 1.85$, $\lambda = 1.0$, $r_0 = 0.1$ (*c*). Phases: I = isotropic, N = nematic, SmA = smectic A, Cr = crystal.

$C = 1.5$, $\lambda = 1.0$, $r_0 = 0.15$; the full I–N–SmA–Cr sequence (*b*) is obtained for the set $T_1 = 0.9$, $T_2 = 0.8$, $\alpha_1 = 0.5$, $\alpha_2 = 0.25$, $C = 1.5$, $\lambda = 1.0$, $r_0 = 0.08$; and the I–SmA–Cr sequence is obtained for the set $T_1 = 0.9$, $T_2 = 0.825$, $\alpha_1 = 0.5$, $\alpha_2 = 0.25$, $C = 1.85$, $\lambda = 1.0$, $r_0 = 0.1$. For all three cases, smectic A phase shrinks out of existence at high pressures/temperatures. Qualitatively, our figure 4 (*a*) is topologically similar to figure 14 (*a*) of [13], and figure 4 (*c*) is topologically similar to their figure 14 (*b*). Thus, we can say that the case where smectic phase is absent at low pressures corresponds to less anisotropic particles, and the case where nematic is absent at low pressures, corresponds to more anisotropic particles. However, more studies (both theoretical and numerical) are needed to support this claim.

The phase diagrams shown in figures 2–4 encompass most of the topologies that can be constructed from the four phases (I, N, SmA and Cr) under consideration.

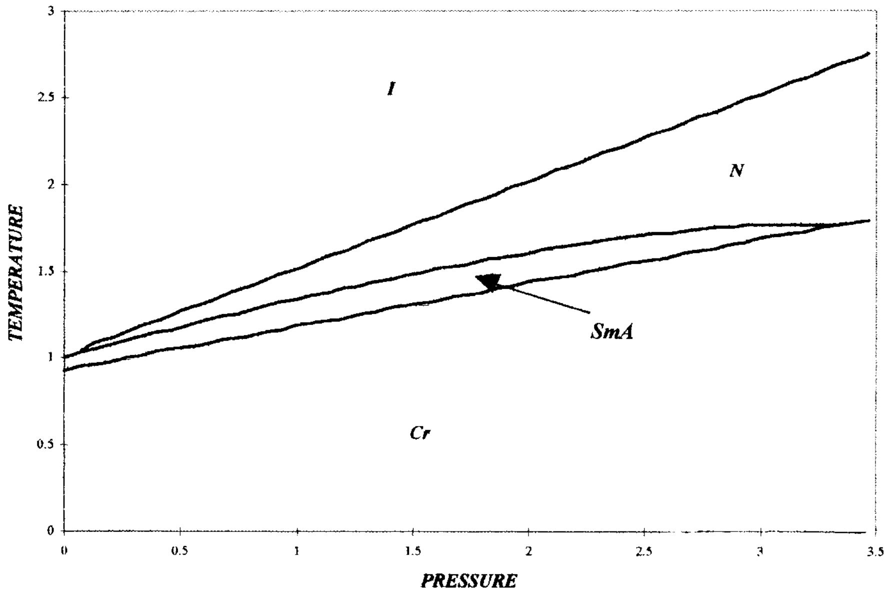


Figure 4. (*continued*). (*c*)

They also help shed light on the role of pressure in stabilizing or destabilizing the liquid crystalline phases—a question which may be important for polymeric or colloidal liquid crystals where mechanical fields often play a significant role in determining thermodynamic properties.

4. Discussion

We have developed a phenomenological free energy expression to describe a spectrum of topologies of the crystal—liquid crystal phase diagram for uniaxial materials. The proposed free energy allows for all observed topologies of the phase diagram that includes isotropic, nematic, smectic A, and crystal phases. It also includes a plastic solid phase, which may be seen for systems with a very weak anisotropy (we do not consider it in detail in this study).

To understand better the behaviour of different anisotropic liquids we calculated pressure–temperature phase diagrams for several model systems. Three classes of anisotropic systems were studied: E-class systems, which have no smectic phase, G-class systems, which have smectic phase in a finite region of the TP plane, and R-class systems, having smectic phase in an infinite area of the TP plane. Thus, by varying just three parameters of the free energy (6), one can obtain all experimentally observed phase sequences and phase diagrams for liquid crystals without tilted and re-entrant phases. (We did not consider the situations where direct isotropic–crystal transition takes place at low pressures, but such phase diagrams can also be obtained using free energy (6)—in these cases, liquid crystal phases may appear at higher pressures.)

One of the immediate questions posed by this theory is the nature of the nematic–smectic A (N–SmA) transition. It is established that the N–SmA transition is continuous [26] unless it is very close to the nematic–isotropic (N–I) transition, in which case it becomes first order. More detailed theoretical studies of the N–SmA transition suggested (see, e.g. [27, 28]) that fluctuations of the orientational order parameter cause it to become a very weakly first order transition. In our theory, the N–SmA transition is always first order; however, it is always a very weak first order, because the cubic term coefficient $r_0 - r$ is small compared with the fourth order term. Thus, the behaviour of entropy, heat capacity and order parameters at N–SmA transition should not be very different from that observed experimentally.

Because the single Landau free energy is used to describe a whole region of liquid crystalline phases, it is clear that the theory is limited to systems with relatively weak anisotropies and relatively narrow liquid crystal phases. If a nematic or smectic phase becomes very broad the Landau free energy becomes inaccurate and it is necessary to use higher-order terms in the free energy expansion in powers of order parameters S and m.

The proposed theory can be a useful tool in a practical description of the thermodynamics of liquid crystals. Because of its simplicity and flexibility it can be instrumental in connecting results of realistic molecular modelling and/or calculation using strict molecular theory like DFT with experimental data. It can also be easily extended to binary mixtures and to homological series. Its simplicity also suggests that it can be further expanded to include liquid crystalline phases such as tilted smectics.

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