A phase-field-crystal model for liquid crystals

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Abstract
On the basis of static and dynamical density functional theory, a phase-field-crystal model is
derived which involves both the translational density and the orientational degree of ordering as
well as a local director field. The model exhibits stable isotropic, nematic, smectic A, columnar,
plastic–crystalline and orientationally ordered crystalline phases. As far as the dynamics is
concerned, the translational density is a conserved order parameter while the orientational
ordering is non-conserved. The derived phase-field-crystal model can serve for use in efficient
numerical investigations of various nonequilibrium situations in liquid crystals.

1. Introduction

Within the phase-field-crystal (PFC) model [1–3] the crystalline density field is described basically in terms of a single Fourier mode, i.e. as a sinusoidal density wave. The PFC model can be understood as a modified Landau expansion of the full inhomogeneous one-particle density field of the solid. It has been applied for large-scale numerical investigations of dynamics in the solid state. Characteristic examples include calculations of a variety of different quantities: the structure and free energy of the fluid crystal interface [4, 5], crystal growth dynamics into a supercooled liquid [6], the structure [7] and dynamics [8] of grain boundaries, and the Asaro–Tiller–Grinfeld instability [9–12]. A solid particle just enters as a 'blob', i.e. a weak density modulation, and the dynamics is diffusive on long timescales, i.e. the density itself is a conserved order parameter.

Recently, the PFC model was derived from dynamical density functional theory (DDFT) [13–16]. Static density functional theory provides a microscopic framework to describe crystallization in equilibrium [17–20] and a Landau expansion in terms of density modulations [21–24] can be used to derive the corresponding approximative free energy for the PFC. Density functional theory was generalized towards nonequilibrium dynamics for Brownian systems [25–27] and the resulting dynamical density functional theory can be used to derive the dynamics of the PFC [16]. First of all, this derivation should apply to colloidal dispersions whose short-time dynamics is clearly diffusive. But also molecular systems governed by Newtonian dynamics for short times behave diffusive on longer timescales and therefore the derivation might have relevance for atomic systems as well.

The PFC model has been generalized to mixtures by including more than a single density field [24]. However, it has never been applied to liquid crystals which are made by particles with *orientational degrees of freedom*[1]. Under appropriate thermodynamic conditions, these particles occur in liquid–crystalline phases including nematic, smectic A, columnar, and plastic–crystalline phases [29, 30]. While the DDFT approach was recently generalized towards orientational dynamics for Brownian rods both in three [31] and two [32] dimensions, the link towards the PFC model has not yet been elaborated for orientational degrees of freedom.

In this paper, we close this gap and propose a PFC model for liquid–crystalline phases. One motivation here is to propose a minimal model, i.e. the simplest nontrivial model for dynamics of liquid crystals. We derive this model from dynamical density functional theory. Depending on the model parameters, the resulting model does accommodate isotropic, nematic, smectic A, columnar, plastic–crystalline phase and an orientational ordered crystal. It can therefore be used to describe the statics and nonequilibrium dynamics in various situations where these phases are relevant. This may stimulate further numerical investigations. The model is basically formulated in terms of two density fields, a translational and an orientational one, plus a local director field. While the translational density field is conserved, the orientational one and the director field are non-conserved and relax quicker.

The paper is organized as follows: in section 2, we derive the PFC model from fluid-based density functional theory by expanding the orientational dependence of the density field

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[1] The only recent application of PFC theory is to anisotropic particles with a fixed orientation, see [28].

up to the first nontrivial order and performing a gradient expansion in the translational coordinate. Then, in section 3, we discuss the parameter space for which stability of the different phases is obtained. The dynamical equations are derived from dynamical density functional theory in section 4. We then discuss possible extensions of the model to more complicated situations and give final conclusions in section 5.

2. Derivation of the phase-field-crystal model for liquid crystals: statics

We start our derivation from microscopic static density functional theory for liquid crystals. We consider N particles with orientational degrees of freedom described by a set of unit vectors $\{\hat{u}_i; i = 1, \ldots, N\}$ and center-of-mass positions $\{\vec{R}_i; i = 1, \ldots, N\}$. Though most of the considerations can be done in three-dimensional space, we restrict ourselves in the following to two spatial dimensions, where $\vec{R}_i \in \mathbb{R}^2$ and $\hat{u}_i(\phi) = (\cos\phi, \sin\phi)$ ($\phi \in [0, 2\pi[$). The system has a total area A and is kept at finite temperature T.

A pair interaction potential $V(\vec{R}_1 - \vec{R}_2, \hat{u}_1, \hat{u}_2)$ between two particles 1 and 2 is assumed. We henceforth consider *apolar* particles implying the following symmetries

$$V(\vec{r}, \hat{u}_1, \hat{u}_2) = V(-\vec{r}, \hat{u}_1, \hat{u}_2) = V(\vec{r}, -\hat{u}_1, \hat{u}_2)$$
$$= V(\vec{r}, \hat{u}_1, -\hat{u}_2) = V(\vec{r}, \hat{u}_2, \hat{u}_1). \tag{1}$$

Examples for $V(\vec{R}_1 - \vec{R}_2, \hat{u}_1, \hat{u}_2)$ comprise: (i) excluded volume interactions as dictated by hard spherocylinders [30, 33] or hard ellipsoids [34] which are used for sterically stabilized colloids, (ii) Yukawa segment models [35–37] used for charged colloidal rods. (iii) Gay-Berne potentials [38–40] used for molecular liquid crystals.

The inhomogeneous one-particle density $\rho(\vec{R}, \hat{u})$ provides the joint probability density to find particles at center-of-mass position $\vec{R}$ with orientation $\hat{u}$.

$$\rho(\vec{R}, \hat{u}) = \left\langle \sum_{i=1}^{N} \delta(\vec{R} - \vec{R}_i)\delta(\phi - \phi_i) \right\rangle \tag{2}$$

where for an observable $\mathcal{A}$

$$\langle \mathcal{A} \rangle = \frac{1}{Z} \int_A d^2 R_1 \cdots \int_A d^2 R_N \int_0^{2\pi} d\phi_1 \cdots \int_0^{2\pi} d\phi_N$$
$$\times \mathcal{A} \exp\left[-\sum_{i,j=1; i \neq j}^{N} \frac{V(\vec{R}_i - \vec{R}_j, \hat{u}_i, \hat{u}_j)}{k_B T} \right] \tag{3}$$

is the normalized canonical average, k_B denoting Boltzmann's constant, and the classical canonical partition function Z ensures the normalization $\langle 1 \rangle = 1$. Clearly, for apolar particles, $\rho(\vec{R}, \hat{u}) = \rho(\vec{R}, -\hat{u})$.

Classical density functional theory of inhomogeneous fluids now provides the existence of an excess free energy density functional such that the functional

$$\Omega(T, A, \mu, [\rho(\vec{R}, \hat{u})]) = \mathcal{F}_{id}(T, A, [\rho(\vec{R}, \hat{u})])$$
$$+ \mathcal{F}_{exc}(T, A, [\rho(\vec{R}, \hat{u})]) - \int_A d^2 R \int_0^{2\pi} d\phi \mu \rho(\vec{R}, \hat{u}) \tag{4}$$

is minimal for the equilibrium density field for a given chemical potential μ, temperature T and area A. The ideal rotator gas functional $\mathcal{F}_{id}$ is known exactly:

$$\mathcal{F}_{id}(T, A, [\rho(\vec{R}, \hat{u})]) = k_B T \int_A d^2 R \int_0^{2\pi} d\phi \, \rho(\vec{R}, \hat{u}(\phi))$$
$$\times [\ln(\Lambda^2 \rho(\vec{R}, \hat{u}(\phi))) - 1], \tag{5}$$

where Λ denotes the (irrelevant) thermal wavelength. The excess free energy functional $\mathcal{F}_{exc}(T, A, [\rho(\vec{R}, \hat{u})])$, on the other hand, incorporates all correlations and is not known in general. In the low density limit, a second virial approximation (Onsager functional) is getting asymptotically exact [29]

$$\mathcal{F}_{exc}(T, A, [\rho(\vec{R}, \hat{u})]) \approx \frac{1}{2} \int_A d^2 R_1 \int_A d^2 R_2 \int_0^{2\pi} d\phi_1$$
$$\times \int_0^{2\pi} d\phi_2 \left(\exp\left(-\frac{V(\vec{R}_1 - \vec{R}_2, \hat{u}_1, \hat{u}_2)}{k_B T} \right) - 1 \right)$$
$$\times \rho(\vec{R}_1, \hat{u}_1)\rho(\vec{R}_2, \hat{u}_2). \tag{6}$$

More generally, the Ramakrishnan–Yussouff theory of freezing [17] can be applied to get the following perturbative approximation for $\mathcal{F}_{exc}$

$$\mathcal{F}_{exc}(T, A, [\rho(\vec{R}, \hat{u})]) \approx -\frac{k_B T}{2} \int_A d^2 R_1 \int_A d^2 R_2 \int_0^{2\pi} d\phi_1$$
$$\times \int_0^{2\pi} d\phi_2 c^{(2)}(\vec{R}_1 - \vec{R}_2, \hat{u}_1, \hat{u}_2)(\rho(\vec{R}_1, \hat{u}_1) - \bar{\rho})$$
$$\times (\rho(\vec{R}_2, \hat{u}_2) - \bar{\rho}) \tag{7}$$

which can be viewed as a truncated density expansion in the density difference $\rho(\vec{R}_1, \hat{u}_1) - \bar{\rho}$ around a mean density $\bar{\rho}$ with the kernel representing the direct correlation function of the reference fluid at temperature T and density $\bar{\rho}$.

Another expression which works complementary at high density for very soft interactions [31] is a mean-field approximation

$$\mathcal{F}_{exc}(T, A, [\rho(\vec{R}, \hat{u})]) \approx \frac{1}{2} \int_A d^2 R_1 \int_A d^2 R_2 \int_0^{2\pi} d\phi_1$$
$$\times \int_0^{2\pi} d\phi_2 V(\vec{R}_1 - \vec{R}_2, \hat{u}_1, \hat{u}_2)\rho(\vec{R}_1, \hat{u}_1)\rho(\vec{R}_2, \hat{u}_2). \tag{8}$$

More accurate forms for $\mathcal{F}_{exc}$ have been proposed for hard particles using weighted density approximations [41, 42] or fundamental-measure theory [20].

In the following we shall adopt the Ramakrishnan–Yussouff theory and approximate further by only considering weak anisotropies in the orientations. The leading expression in the density parametrization is then

$$\rho(\vec{R}, \hat{u}) = \bar{\rho} + \bar{\rho}\psi_1(\vec{r}) + \bar{\rho}\psi_2(\vec{r})\left((\hat{u} \cdot \hat{u}_0(\vec{r}))^2 - \frac{1}{2}\right) + \cdots. \tag{9}$$

Here, the real-valued dimensionless orientationally averaged density is $\psi_1(\vec{r})$ which is identical to the original treatment of the PFC model [1, 2]. The dimensionless field $\psi_2(\vec{r})$, on the other hand, measures the local degree of orientational order. For apolar particles, the leading anisotropic contribution is the third term on the right-hand side of equation (9). Finally, the field $\hat{u}_0(\vec{r})$ defines the local director of the orientational field[2].

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[2] As an equivalent description, a position-dependent nematic tensor could be used in the density parametrization instead of using the fields $\psi_2(\vec{r})$ and $\hat{u}_0(\vec{r})$. This notation has formal advantages and could be helpful in order to derive generalizations of the present model to three spatial dimensions.

We now derive the static free energy functional. With

$$x = \psi_1 + \psi_2 P_2(\hat{u} \cdot \hat{u}_0) \qquad (10)$$

where $P_2(y) = y^2 - \frac{1}{2}$, the ideal rotator gas part reads as

$$\mathcal{F}_{\mathrm{id}} = k_{\mathrm{B}} T \bar{\rho} \int_A \mathrm{d}^2 R \int_0^{2\pi} \mathrm{d}\phi (1+x)[\ln(\Lambda^2 \bar{\rho}(1+x)) - 1]$$

$$= F_0 + k_{\mathrm{B}} T \bar{\rho} \int_A \mathrm{d}^2 R \int_0^{2\pi} \mathrm{d}\phi$$

$$\times (\tfrac{1}{2}x^2 - \tfrac{1}{6}x^3 + \tfrac{1}{12}x^4 + \mathcal{O}(x^5)) \qquad (11)$$

where $F_0 = 2\pi A k_{\mathrm{B}} T \bar{\rho}(\ln(\Lambda^2 \bar{\rho}) - 1)$ and irrelevant terms linear in x on the right-hand side of equation (11) were absorbed in a scaled chemical potential. Inserting (10) and performing the angular average, we obtain

$$\mathcal{F}_{\mathrm{id}}[\psi_1, \psi_2, \hat{u}_0] = F_0 + \bar{\rho} k_{\mathrm{B}} T \pi \int_A \mathrm{d}^2 R \left\{ \psi_1^2 + \frac{\psi_2^2}{8} \right.$$

$$\left. - \frac{\psi_1^3}{3} - \frac{\psi_1 \psi_2^2}{8} + \frac{\psi_1^4}{6} + \frac{\psi_1^2 \psi_2^2}{8} + \frac{\psi_2^4}{256} \right\}. \qquad (12)$$

The correlational part within the Ramakrishnan–Yussouff approximation is

$$\mathcal{F}_{\mathrm{exc}} = -\frac{k_{\mathrm{B}} T \bar{\rho}^2}{2} \int_A \mathrm{d}^2 R_1 \int_A \mathrm{d}^2 R_2 \int_0^{2\pi} \mathrm{d}\phi_1 \int_0^{2\pi} \mathrm{d}\phi_2$$

$$\times (\psi_1(\vec{R}_1) + \psi_2(\vec{R}_1) P_2(\hat{u}(\phi_1) \cdot \hat{u}_0(\vec{R}_1)))$$

$$\times (\psi_1(\vec{R}_2) + \psi_2(\vec{R}_2) P_2(\hat{u}(\phi_2) \cdot \hat{u}_0(\vec{R}_2)))$$

$$\times c^{(2)}(\vec{R}_1 - \vec{R}_2, \phi_1, \phi_2). \qquad (13)$$

We now decompose

$$c(\vec{R}, \phi_1, \phi_2) = \sum_{m=-\infty}^{\infty} \sum_{m'=-\infty}^{\infty} c_{mm'}(\vec{R}) \mathrm{e}^{2\mathrm{i}m\phi_1} \mathrm{e}^{2\mathrm{i}m'\phi_2} \qquad (14)$$

and consider only the leading terms where $m, m' \in \{-1, 0, 1\}$. The relevant expansion coefficients are

$$c_{mm'}(\vec{R}) = \frac{1}{(2\pi)^2} \int_0^{2\pi} \mathrm{d}\phi \int_0^{2\pi} \mathrm{d}\phi' \mathrm{e}^{-2\mathrm{i}m\phi} \mathrm{e}^{-2\mathrm{i}m'\phi'} c^{(2)}$$

$$\times (\vec{R}, \phi, \phi'). \qquad (15)$$

By symmetry, it can be shown that $c_{00}(\vec{R})$, $c_{-11}(\vec{R})$ and $c_{1-1}(\vec{R})$ only depend on $|\vec{R}|$. Therefore

$$\mathcal{F}_{\mathrm{exc}} = -\frac{k_{\mathrm{B}} T \bar{\rho}^2}{2} \int_A \mathrm{d}^2 R_1 \int_A \mathrm{d}^2 R_2 4\pi^2 [c_{00}(|\vec{R}_1 - \vec{R}_2|)$$

$$\times \psi_1(\vec{R}_1)\psi_1(\vec{R}_2) + \tfrac{1}{4}\psi_1(\vec{R}_1)\psi_2(\vec{R}_2)\{c_{0-1}(\vec{R}_1 - \vec{R}_2)$$

$$\times \mathrm{e}^{-2\mathrm{i}\phi_0(\vec{R}_2)} + c_{01}(\vec{R}_1 - \vec{R}_2)\mathrm{e}^{2\mathrm{i}\phi_0(\vec{R}_2)}\} + \tfrac{1}{4}\psi_1(\vec{R}_2)\psi_2(\vec{R}_1)$$

$$\times \{c_{-10}(\vec{R}_1 - \vec{R}_2)\mathrm{e}^{-2\mathrm{i}\phi_0(\vec{R}_1)} + c_{10}(\vec{R}_1 - \vec{R}_2)\mathrm{e}^{2\mathrm{i}\phi_0(\vec{R}_1)}\}$$

$$+ \tfrac{1}{16}\psi_2(\vec{R}_1)\psi_2(\vec{R}_2)\{c_{-1-1}(\vec{R}_1 - \vec{R}_2)\mathrm{e}^{-2\mathrm{i}\phi_0(\vec{R}_1)-2\mathrm{i}\phi_0(\vec{R}_2)}$$

$$+ c_{-11}(|\vec{R}_1 - \vec{R}_2|)\mathrm{e}^{-2\mathrm{i}\phi_0(\vec{R}_1)+2\mathrm{i}\phi_0(\vec{R}_2)}$$

$$+ c_{1-1}(|\vec{R}_1 - \vec{R}_2|)\mathrm{e}^{2\mathrm{i}\phi_0(\vec{R}_1)-2\mathrm{i}\phi_0(\vec{R}_2)}$$

$$+ c_{11}(\vec{R}_1 - \vec{R}_2)\mathrm{e}^{2\mathrm{i}\phi_0(\vec{R}_1)+2\mathrm{i}\phi_0(\vec{R}_2)}\}]. \qquad (16)$$

Now a gradient expansion is performed [24] up to fourth order in the $\psi_1 \psi_1$ term of equation (16) and up to second order in the

$\psi_1 \psi_2$ and $\psi_2 \psi_2$ terms. We assume that the highest gradient term ensures stability. Thereby one obtains

$$\mathcal{F}_{\mathrm{exc}} = \mathcal{F}_{\mathrm{exc}}^{(1)} + \mathcal{F}_{\mathrm{exc}}^{(2)} + \mathcal{F}_{\mathrm{exc}}^{(3)} \qquad (17)$$

with

$$\frac{\mathcal{F}_{\mathrm{exc}}^{(1)}}{k_{\mathrm{B}} T} = 2\pi^2 \bar{\rho} \int_A \mathrm{d}^2 R [A\psi_1^2(\vec{R}) - B(\vec{\nabla}\psi_1(\vec{R}))^2$$

$$+ C(\Delta \psi_1(\vec{R}))^2] \qquad (18)$$

and

$$\frac{\mathcal{F}_{\mathrm{exc}}^{(2)}}{k_{\mathrm{B}} T} = 2\pi^2 \bar{\rho} \int_A \mathrm{d}^2 R [D\psi_2^2(\vec{R}) + E\{(\vec{\nabla}\psi_2(\vec{R}))^2$$

$$+ 4\psi_2^2(\vec{R})(\vec{\nabla}\phi_0(\vec{R}))^2\}] \qquad (19)$$

and

$$\frac{\mathcal{F}_{\mathrm{exc}}^{(3)}}{k_{\mathrm{B}} T} = 2\pi^2 \bar{\rho} \int_A \mathrm{d}^2 R F[(\vec{\nabla}\psi_1(\vec{R})) \cdot (\vec{\nabla}\psi_2(\vec{R}))$$

$$+ 2\psi_2(\vec{R})(\hat{u}_0(\vec{R}) \cdot \vec{\nabla})^2 \psi_1(\vec{R})]. \qquad (20)$$

In detail, in (20), $(\hat{u}_0(\vec{R}) \cdot \vec{\nabla})^2 := \sum_{i,j=1}^2 u_{0i}(\vec{R})u_{0j}(\vec{R})\partial_i \partial_j$ where $u_{0i}(\vec{R}) = \left(\begin{smallmatrix} \cos\phi_0(\vec{R}) \\ \sin\phi_0(\vec{R}) \end{smallmatrix} \right)_i$.

In (18)–(20), the coefficients A, B, C, D, E and F are generalized moments of the direct correlation function. In general, they depend on the thermodynamic conditions $(T, \bar{\rho})$. In detail[3] (for $A = \mathbb{R}^2$),

$$A = -2\pi \bar{\rho} \int_0^\infty \mathrm{d}R\, R c_{00}(R) \qquad (21)$$

$$B = \pi \bar{\rho} \int_0^\infty \mathrm{d}R\, R^3 c_{00}(R) \qquad (22)$$

$$C = -\frac{\pi \bar{\rho}}{12} \int_0^\infty \mathrm{d}R\, R^5 c_{00}(R) \qquad (23)$$

$$D = -\frac{\pi \bar{\rho}}{4} \int_0^\infty \mathrm{d}R\, R c_{-11}(R) \qquad (24)$$

$$E = \pi \bar{\rho} \int_0^\infty \mathrm{d}R\, R^3 c_{-11}(R) \qquad (25)$$

$$F = -\frac{\pi}{8} \int_0^\infty \mathrm{d}R\, R^3 c_{01}(R\cos\phi_R, R\sin\phi_R)\mathrm{e}^{2\mathrm{i}\phi_R}. \qquad (26)$$

As a remark: F does not depend on ϕ_R. For stability reasons, we henceforth assume $C, E > 0$.

Let us now discuss the static free energy functional. In the limit of no orientational order, $\psi_2 \equiv 0$, one recovers the phase-field-crystal model of Elder et al [1, 2]. The expansion up to fourth order is formally similar to a Landau expansion of the smectic A–isotropic phase transition if ψ_1 represents the smectic order parameter [43]. In the opposite case of constant ψ_1 and constant ψ_2, Frank's elastic energy with a nonvanishing splay and vanishing bend modulus is recovered in the term $\sim (\vec{\nabla}\phi_0(\vec{R}))^2$ in (19). In fact, in two spatial dimensions there are only two Frank elastic constants since the twist modulus vanishes. If ψ_1 is constant and both ψ_2 and $\hat{u}_0$ are space dependent, we obtain the Landau–de Gennes free energy [44]

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[3] These coefficients can also be fitted to the correlation function at nonzero wavevector resulting in effective fit parameters.

Table 1. Characteristic values for the number density ψ_1, the nematic order parameter ψ_2 and the director field $\hat{u}_0$ for six different liquid–crystalline phases, namely isotropic, nematic, plastic–crystalline, orientationally ordered crystalline, smectic A and columnar.

Liquid–crystalline phase	ψ_1	ψ_2	$\hat{u}_0$
Isotropic	0	0	Irrelevant
Nematic	Constant	$\neq 0$	Constant
Plastic–crystalline	Oscillatory	0	Irrelevant
Orientationally ordered crystalline	Oscillatory	$\neq 0$	Constant or oscillatory
Smectic A	Planar oscillatory	$\neq 0$	Constant, oscillatory $\parallel \vec{\nabla}\psi_1$
Columnar	Planar oscillatory	$\neq 0$	Constant, oscillatory $\perp \vec{\nabla}\psi_1$

used for inhomogeneous uniaxial nematics. In two dimensions, the Landau–de Gennes free energy has only one gradient coefficient [45] which is again the parameter E. For space-dependent ψ_1 and $\hat{u}_0$, but constant ψ_2, the free energy derived by Pleiner and Brand [46] is recovered. Finally, for space-dependent ψ_1 and ψ_2, we obtain the coupling terms in $\mathcal{F}_{\text{exc}}^{(3)}$ proposed by Brand and Pleiner [47]. However, the full free energy functional (17) with fourth order gradients in ψ_1 and the appropriate couplings to ψ_2 and $\hat{u}_0$ is new and constitutes the basic static result of this paper.

3. Equilibrium bulk phase diagram

By minimizing the free energy functional, for given thermodynamic parameters T and $\bar{\rho}$, the equilibrium phase diagram is gained. In the special case of $\psi_2 = 0$, the PFC phase diagram of Elder *et al* [2] is obtained. By scaling out a length scale, there are only two remaining parameters for which a fluid, a triangular phase and an (unphysical) stripe phase is stable (see figure 4 in [2]). For $D < -\frac{\pi}{4}$, a nonzero stable value for ψ_2 occurs. Combined with the PFC phase diagram, the possibility of a nematic phase and an orientationally ordered crystal emerges. The stripe phase at $\psi_2 \neq 0$ becomes either a smectic A or columnar phase depending on the sign of the parameter F. In fact, it was already shown in [48] that an Onsager functional yields a smectic A phase.

All the possible liquid–crystalline phases are summarized in table 1 together with their characterizing values for the number density ψ_1, the nematic order parameter ψ_2 and the director field $\hat{u}_0$. For $D > -\frac{\pi}{8}$, a plastic crystal and the ordinary isotropic phase can be stable. The full numerical calculation of the equilibrium phase diagram as a function of the parameters A, B, C, E, and F is planned in a future study.

4. Derivation of the phase-field-crystal model for liquid crystals: dynamics

4.1. Dynamical density functional theory

In two spatial dimensions, the dynamical density functional theory for Brownian systems is a deterministic equation for the time-dependent one-particle density field $\rho(\vec{R}, \hat{u}, t)$ [32]:

$$\frac{\partial \rho(\vec{R}, \hat{u}, t)}{\partial t} = \vec{\nabla}^T \cdot D_{\text{T}} \cdot \left(\frac{\rho(\vec{R}, \hat{u}, t)}{k_{\text{B}}T} \vec{\nabla} \frac{\delta \mathcal{F}}{\delta \rho(\vec{R}, \hat{u}, t)} \right)$$
$$+ D_{\text{R}} \frac{\partial}{\partial \phi} \left(\frac{\rho(\vec{R}, \hat{u}, t)}{k_{\text{B}}T} \frac{\partial}{\partial \phi} \frac{\delta \mathcal{F}}{\delta \rho(\vec{R}, \hat{u}, t)} \right). \quad (27)$$

Here, D_{T} is the diagonal translational short-time diffusion tensor which we assume to be isotropic in the following, $D_{\text{T}} = \text{diag}(D_{\text{T}}, D_{\text{T}})$, and D_{R} is the rotational diffusion constant. Furthermore, $\mathcal{F} = \mathcal{F}_{\text{id}} + \mathcal{F}_{\text{exc}}$ is the total free energy functional. If the density parametrization (9) is used, this becomes a functional $\mathcal{F}[\psi_1(\vec{R}), \psi_2(\vec{R}), \phi_0(\vec{R})]$ of the three scalar fields $\psi_1(\vec{R}), \psi_2(\vec{R}), \phi_0(\vec{R})$. Now the chain rule of functional differentiation yields:

$$\frac{\delta \mathcal{F}}{\delta \rho(\vec{R}, \phi)} = \frac{1}{2\pi \bar{\rho}} \frac{\delta \mathcal{F}}{\delta \psi_1(\vec{R})} + \frac{4}{\pi \bar{\rho}} \frac{\delta \mathcal{F}}{\delta \psi_2(\vec{R})} P_2(\cos(\phi - \phi_0(\vec{R})))$$
$$+ \frac{1}{\pi \bar{\rho}} \frac{\delta \mathcal{F}}{\delta \phi_0(\vec{R})} \frac{\sin(2(\phi - \phi_0(\vec{R})))}{\psi_2(\vec{R})}. \quad (28)$$

By inserting this into equation (27), coupled equations of motion can be obtained.

4.2. Derivation of the dynamics (PFC1 model)

First we describe the dynamics for the most case which is called PFC1 model in [16]. The PFC1 model avoids two further approximations, namely the expansion of the logarithm (11) and a constant mobility assumption. By inserting the chain rule (28) into the dynamical density functional theory (27), one obtains dynamical equations for the three scalar fields $\psi_1(\vec{R}, t)$, $\psi_2(\vec{R}, t)$ and $\phi_0(\vec{R}, t)$ as follows:

$$k_{\text{B}}T\bar{\rho}\dot{\psi}_1 = k_{\text{B}}T\bar{\rho}D_{\text{T}}\Delta\psi_1 + \frac{D_{\text{T}}}{\pi}\left(\frac{1}{2}\vec{\nabla}\left((1+\psi_1)\vec{\nabla}\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\psi_1} \right.\right.$$
$$\left.\left. - \frac{\delta\mathcal{F}_{\text{exc}}}{\delta\phi_0}\vec{\nabla}\phi_0 + \psi_2\vec{\nabla}\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\psi_2} \right) \right) \quad (29)$$

$$k_{\text{B}}T\bar{\rho}\dot{\psi}_2 = k_{\text{B}}T\bar{\rho}(D_{\text{T}}\Delta\psi_2 - 4D_{\text{R}}\psi_2 - 4D_{\text{T}}\psi_2(\vec{\nabla}\phi_0)^2)$$
$$+ \frac{D_{\text{T}}}{\pi}\left(\vec{\nabla}\left(4(1+\psi_1)\left(\vec{\nabla}\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\psi_2} - \frac{\delta\mathcal{F}_{\text{exc}}}{\delta\phi_0}\frac{\vec{\nabla}\phi_0}{\psi_2} \right) \right.\right.$$
$$\left. + \frac{\psi_2}{2}\vec{\nabla}\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\psi_1} \right) + (1+\psi_1)\left(-16\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\psi_2}(\vec{\nabla}\phi_0)^2 \right.$$
$$\left.\left. - 4\vec{\nabla}\left(\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\phi_0}\frac{1}{\psi_2} \right)\vec{\nabla}\phi_0 \right) \right) - \frac{D_{\text{R}}}{\pi}\left(16(1+\psi_1)\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\psi_0} \right) \quad (30)$$

$$k_{\text{B}}T\bar{\rho}\psi_2\dot{\phi}_0 = k_{\text{B}}T\bar{\rho}(D_{\text{T}}\psi_2\Delta\phi_0 + 2D_{\text{T}}(\vec{\nabla}\psi_2 \cdot \vec{\nabla}\phi_0))$$
$$+ \frac{D_{\text{T}}}{\pi}\left[\left(4(1+\psi_1)\left(\vec{\nabla}\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\psi_2} - \frac{\delta\mathcal{F}_{\text{exc}}}{\delta\phi_0}\frac{\vec{\nabla}\phi_0}{\psi_2} \right) \right.\right.$$
$$+ \frac{\psi_2}{2}\vec{\nabla}\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\psi_1} \right)\vec{\nabla}\phi_0 + \vec{\nabla}\left((1+\psi_1)\left(4\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\psi_2}\vec{\nabla}\phi_0 \right.\right.$$
$$\left.\left.\left. + \vec{\nabla}\left(\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\phi_0}\frac{1}{\psi_2} \right) \right) \right) \right] - \frac{D_{\text{R}}}{\pi}\left(4(1+\psi_1)\frac{\delta\mathcal{F}_{\text{exc}}}{\delta\phi_0}\frac{1}{\psi_2} \right). \quad (31)$$

The right-hand side of equation (30) clearly shows that the time-derivative $\dot{\psi}_1$ is proportional to a divergence of a generalized current. This implies that a generalized continuity

equation holds such that the order parameter field $\psi_1(\vec{R}, t)$ is conserved. On the other hand, this is not true for the two remaining orientational order parameter fields $\psi_2(\vec{R}, t)$ and $\phi_0(\vec{R}, t)$ which are therefore non-conserved.

The functional derivatives are local and given by

$$\frac{1}{4\pi^2 k_{\mathrm{B}} T \bar{\rho}} \frac{\delta \mathcal{F}_{\mathrm{exc}}}{\delta \psi_1} = A\psi_1 + B\Delta\psi_1 + C\Delta^2\psi_1$$
$$- \frac{F}{2}\Delta\psi_2 + F\sum_{i,j=1}^{2} \partial_i\partial_j(\psi_2 u_{0i} u_{0j}), \qquad (32)$$

$$\frac{1}{4\pi^2 k_{\mathrm{B}} T \bar{\rho}} \frac{\delta \mathcal{F}_{\mathrm{exc}}}{\delta \psi_2} = D\psi_2 - E\Delta\psi_2 + 4E\psi_2(\vec{\nabla}\phi_0)^2$$
$$- \frac{F}{2}\Delta\psi_1 + F\sum_{i,j=1}^{2} u_{0i} u_{0j}\partial_i\partial_j\psi_1, \qquad (33)$$

$$\frac{1}{4\pi^2 k_{\mathrm{B}} T \bar{\rho}} \frac{\delta \mathcal{F}_{\mathrm{exc}}}{\delta \phi_0} = -4E\psi_2^2\Delta\phi_0 + F\psi_2$$
$$\times \sum_{i,j=1}^{2} \frac{\partial u_{0i} u_{0j}}{\partial \phi_0}\partial_i\partial_j\psi_1 \qquad (34)$$

where

$$\frac{\partial u_{0i} u_{0j}}{\partial \phi_0} = \begin{pmatrix} -\sin 2\phi_0 & \cos 2\phi_0 \\ \cos 2\phi_0 & \sin 2\phi_0 \end{pmatrix}_{ij}. \qquad (35)$$

Combining these equations yields explicit deterministic and coupled equations of motion for the three order parameter fields $\psi_1(\vec{R}, t)$, $\psi_2(\vec{R}, t)$ and $\phi_0(\vec{R}, t)$ which can be implemented for a numerical solution.

4.3. Derivation of the phase-field-crystal model with constant mobility (PFC2 model)

In the constant mobility approximation, the prefactor in front of the density functional derivatives on the right-hand side of equation (27) is replaced by the constant $\frac{\bar{\rho}}{k_{\mathrm{B}} T}$. Then the dynamical density functional equations simplify to

$$\frac{\partial \rho(\vec{R}, \hat{u}, t)}{\partial t} = \left(D_{\mathrm{T}}\Delta + D_{\mathrm{R}}\frac{\partial^2}{\partial \phi^2} \right) \frac{\bar{\rho}}{k_{\mathrm{B}} T} \frac{\delta \mathcal{F}}{\delta \rho(\vec{R}, \hat{u}, t)}. \qquad (36)$$

In this case, the equations of motion for the three scalar fields $\psi_1(\vec{R}, t)$, $\psi_2(\vec{R}, t)$ and $\phi_0(\vec{R}, t)$ read as

$$k_{\mathrm{B}} T \pi \bar{\rho} \dot{\psi}_1 = \frac{1}{2} D_{\mathrm{T}}\Delta \frac{\delta \mathcal{F}}{\delta \psi_1} \qquad (37)$$

$$k_{\mathrm{B}} T \pi \bar{\rho} \dot{\psi}_2 = D_{\mathrm{T}}\left[4\Delta\frac{\delta \mathcal{F}}{\delta \psi_2} - 16(\vec{\nabla}\phi_0)^2\frac{\delta \mathcal{F}}{\delta \psi_2} \right.$$
$$\left. - 8\left(\vec{\nabla}\left(\frac{\delta \mathcal{F}}{\delta \phi_0}\frac{1}{\psi_2} \right) \right)\cdot\vec{\nabla}\phi_0 - 4\frac{\delta \mathcal{F}}{\delta \phi_0}\frac{\Delta\phi_0}{\psi_2} \right] - 16 D_{\mathrm{R}}\frac{\delta \mathcal{F}}{\delta \psi_2} \qquad (38)$$

and finally

$$k_{\mathrm{B}} T \pi \bar{\rho} \psi_2 \dot{\phi}_0 = D_{\mathrm{T}}\left[8\left(\vec{\nabla}\frac{\delta \mathcal{F}}{\delta \psi_2} \right)\vec{\nabla}\phi_0 + 4\frac{\delta \mathcal{F}}{\delta \psi_2}\Delta\phi_0 \right.$$
$$\left. + \Delta\left(\frac{\delta \mathcal{F}}{\delta \phi_0}\frac{1}{\psi_2} \right) - 4\frac{\delta \mathcal{F}}{\delta \phi_0}\frac{1}{\psi_2}\left(\vec{\nabla}\phi_0 \right)^2 \right] - 4 D_{\mathrm{R}}\frac{1}{\psi_2}\frac{\delta \mathcal{F}}{\delta \phi_0}. \qquad (39)$$

The ordinary phase-field-crystal model is obtained by a subsequent expansion of the ideal rotator term (11) up to fourth order. Following [16], the resulting dynamics is called PFC2 model. In this case, the density functional derivatives are again local and given by

$$\frac{1}{k_{\mathrm{B}} T \bar{\rho}} \frac{\delta \mathcal{F}}{\delta \psi_1} = \pi\left(2 + 2\psi_1 - \psi_1^2 - \frac{\psi_2^2}{8} + \frac{2}{3}\psi_1^3 + \frac{\psi_1\psi_2^2}{4} \right)$$
$$+ 4\pi^2\left(A\psi_1 + B\Delta\psi_1 + C\Delta^2\psi_1 - \frac{F}{2}\Delta\psi_2 \right.$$
$$\left. + F\sum_{i,j=1}^{2} \partial_i\partial_j(\psi_2 u_{0i} u_{0j}) \right) \qquad (40)$$

$$\frac{1}{k_{\mathrm{B}} T \bar{\rho}} \frac{\delta \mathcal{F}}{\delta \psi_2} = \pi\left(\frac{\psi_2}{4} - \frac{1}{4}\psi_1\psi_2 + \frac{1}{4}\psi_1^2\psi_2 + \frac{\psi_2^3}{64} \right)$$
$$+ 4\pi^2\left(D\psi_2 - E\Delta\psi_2 + 4E\psi_2(\vec{\nabla}\phi_0)^2 \right.$$
$$\left. - \frac{F}{2}\Delta\psi_1 + F\sum_{i,j=1}^{2} u_{0i} u_{0j}\partial_i\partial_j\psi_1 \right) \qquad (41)$$

$$\frac{1}{k_{\mathrm{B}} T \bar{\rho}} \frac{\delta \mathcal{F}}{\delta \phi_0} = \left(-4E\psi_2^2\Delta\phi_0 + F\psi_2\sum_{i,j=1}^{2} \frac{\partial u_{0i} u_{0j}}{\partial \phi_0}\partial_i\partial_j\psi_1 \right). \qquad (42)$$

The advantage of these equations is that they reduce to the dynamics of the traditional phase-field-crystal model in the pure translational case. For a rough numerical exploration, the PFC2 model should give the same qualitative answer as the PFC1 model. For spherical particles this was shown in [16]. The dynamical equations (37)–(39) represent the main result of this paper.

5. Conclusions

In conclusion, we derived from static and dynamical density functional theory phase-field-crystal equations which govern the diffuse nonequilibrium dynamics for liquid–crystalline phases. Two approximations are involved: first the density functional is approximated by a truncated functional Taylor expansion similar in spirit to the Ramakrishnan–Yussouff theory. Then a generalized gradient expansion in the order parameters is performed which leads to a local density functional. In addition to the traditional scalar phase-field variable ψ_1, a local scalar nematic order parameter ψ_2 and a local nematic director field ϕ_0 was introduced and coupled to the phase-field variable ψ_1. If the additional variables are zero, the phase-field-crystal model of Elder *et al* [1, 2] is recovered. If, on the other hand, ψ_1 is set to zero we recover the Landau–de Gennes free energy for uniaxial nematics extended by Pleiner and Brand [46, 47]. The proposed phase-field-crystal model for liquid crystals allows for a wealth of stable liquid–crystalline phases including isotropic, nematic, smectic A, columnar, plastic–crystalline and orientationally ordered crystals. How the stability of these phases depends in detail on the model parameters still needs to be explored numerically. The new coupled phase-field-crystal equations can be used to simulate the nonequilibrium dynamics of

liquid crystals. Possible problems are dynamics of topological defects in the nematic phase [49] and the formation of metastable phases at a growing interface [50]. As the dynamics in nematic states can be obtained by using other approaches like the one in [47], the present model may be applicable in particular to smectic films and to two-dimensional crystalline phases.

In the present paper, the derivation of the phase-field-crystal model was performed in two spatial dimensions. Though more tedious there is no principle problem in doing the same analysis in three spatial dimensions with the use of spherical harmonics for the orientational degrees of freedom. Moreover the present derivation can in principle be done to higher order in the orientational degrees of freedom. The translational degrees of freedom can be anisotropic for the dynamical mobility matrix[4].

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[4] Finally the present analysis is based on a fluid perturbation theory of the density functional. In principle one can also expand around another phase with a broken symmetry which would result in more general coupling terms than presented here.