

Dynamical field theories for biaxial liquid crystals

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Phase field crystal (PFC) models constitute central tools for a microscopic understanding of the dynamics of complex systems in soft-matter physics. They have found widespread application in the modeling of the uniaxial orientational ordering of liquid crystals. However, only very limited progress has been made in applying them to the more complex cases of biaxial phases and biaxial particles. Here we discuss the microscopic derivation of PFC models for biaxial liquid crystals. We illustrate it by presenting two models, one involving four scalar orientational order parameters relevant for the dynamics of biaxial particles and one involving two scalar order parameters and all three directors to describe biaxial phases in a three-dimensional molecularly uniaxial nematic liquid crystal. These models allow for an efficient simulation of spatially inhomogeneous biaxial orientational ordering dynamics. We also combine our microscopic with a macroscopic approach to extract model coefficients for a full biaxial model from the microscopic derivation for a simple special case. This universal method also enables to perform derivations for other low-symmetry particles where, due to the complexity of the more general cases, this has not been previously attempted.

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I. INTRODUCTION

The study of liquid crystalline ordering phenomena [1] is one of the central areas of soft-matter physics [2–14]. Interest in liquid crystals is motivated both by their rich phase behavior [15,16] and by the possibility of exploiting their intriguing optical properties for a broad range of technological applications [17,18]. Even in the absence of the positional order that is characteristic for an ordinary crystal, liquid crystals can exhibit order-disorder phase transitions due to their orientational degrees of freedom. The most prominent example is the nematic phase where particles preferably align along a common axis, which can be easily manipulated by external fields. The properties of liquid crystals motivating research on them gain additional significance in liquid crystals where the phase or the particle interactions are not axially symmetric. Biaxial liquid crystals [19] can display considerably more orientational ordered phases [20–31]. Due to experimental advances in synthesizing colloidal particles of nearly arbitrary shape [32–34], liquid crystal phases exhibiting biaxial order have the potential to be translated into further applications.

The dynamics of phase transitions in liquid crystals can be modeled via field theories, for which dynamical density functional theory (DDFT) is a prime example. DDFT, developed in Refs. [35–37] and reviewed in Refs. [38,39], is a microscopic field-theoretical method that allows to model the dynamics of complex fluids by extending results from equilibrium

density functional theory (DFT) to the nonequilibrium case. The application of DDFT to orientational dynamics has a long tradition [40–44]. Usually, these studies assume the state of an individual particle to be determined by a position vector $\mathbf{R}$ and a single orientation vector $\mathbf{m}_3$, which in the three-dimensional case implies that the particles have an axis of continuous rotational symmetry (*uniaxial particles*). The archetypal example for this are rodlike particles. In general, specifying the orientation of a particle without such a symmetry (*biaxial particle*) in three dimensions requires three angles (*Euler angles*) [45]. A DDFT for this case, describing particles with arbitrary shapes, was derived in Refs. [46,47]. DDFT is now a widely used method to model particles with orientational degrees of freedom, with applications that include nematic and smectic liquid crystals [48], deposition of hard spherocylinders [49], protein solvation [50], and active matter [51,52].

Phase field crystal (PFC) models [53,54] offer a simpler, more phenomenological, description than DDFT and can be derived from it via a series of approximations [52,55–57]. PFC models for liquid crystals usually feature one or several orientational order parameters. Work on this topic started in Ref. [58] with the development of a PFC model for nematic liquid crystals in two dimensions. Extensions considering three-dimensional [59] and then polar liquid crystals [60,61] paved the way to active PFC models [62], the most widely used theory of this type which has evolved into one of the central modeling frameworks in active-matter physics [52,63–70].

Most of these PFC studies, however, were limited to particles with uniaxial symmetry and did not consider orientational

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order parameters other than polarization and nematic order. An exception for the two-dimensional case is the recent work by Weigel and Schmiedeberg [71], who derived a PFC model for particles that have an n -fold rotational symmetry. This derivation exploited the fact that one can, in two dimensions, specify the orientation of a particle of an arbitrary shape using just one angle. The very few existing field-theoretical models for the three-dimensional case [46,72], while being very general, are also quite complicated and did therefore not allow for an efficient numerical treatment. Therefore, the study of biaxial liquid crystals in three spatial dimensions would benefit significantly from the development of field-theoretical models that allow to study them in a PFC-type framework.

In this work, we discuss how such models can be derived by combining the derivation strategy employed in Refs. [52,58–61] with the orientational order parameter approach employed in Refs. [31,73]. As specific examples, we then present two models covering important scenarios. First, we obtain a PFC model for liquid crystals consisting of biaxial particles that describes the dynamics of the orientation-averaged density ψ_1 together with the four scalar orientational order parameters S , U , P , and F , as used in earlier treatments of biaxial particles [31,73]. Second, also accounting for the director field dynamics, we obtain a PFC model for phase biaxiality, which generalizes the result of Ref. [59]. This model is obtained with an implicit derivation, as explained in Sec. IV F. Our results can be used for efficient analytical and numerical investigations of orientational ordering dynamics in biaxial liquid crystals. We also develop an efficient method that allows us to arrive at the general full biaxial free energy by combining the restricted microscopic derivation of the first model with a macroscopic approach. This method is also applicable for other symmetry groups and might allow to greatly simplify derivations of the free energy of particles with even lower symmetry (such as chiral particles or bent-core molecules in chiral phases). Thereby, the technique presented here allows us to perform further derivations that have previously not been attempted.

A. Density functional theory

The Hohenberg-Kohn theorem [35,74] states, in the classical case, that there is a unique functional mapping between the one-particle density ρ and the many-body phase-space distribution. This implies the existence of a grand-canonical potential Ω , which is a functional of ρ and which is minimized by the equilibrium density:

$$\frac{\delta \Omega}{\delta \rho(\mathbf{R}, \mathbf{O})} = 0. \quad (1)$$

Here $\mathbf{O}$ denotes the orientation and $\mathbf{R}$ the center-of-mass position of the particles. Via the transformation

$$\Omega = \mathcal{F} + \int d\mathbf{R} \int d\mathbf{O} \rho(\mathbf{R}, \mathbf{O}) (V_{\text{ext}} - \mu), \quad (2)$$

Equation (1) can be translated into the equation

$$\frac{\delta \mathcal{F}}{\delta \rho(\mathbf{R}, \mathbf{O})} = \mu - V_{\text{ext}}, \quad (3)$$

for the free-energy functional $\mathcal{F}$ with external potential V_{ext} and chemical potential μ . Since there exists an analytic representation of the free-energy functional for an ideal gas, given by

$$\mathcal{F}_{\text{id}} = k_B T \int d\mathbf{R} \int d\mathbf{O} (\rho(\mathbf{R}, \mathbf{O}) (\ln(\lambda^3 \rho(\mathbf{R}, \mathbf{O})) - 1)), \quad (4)$$

we can split the free-energy functional

$$\mathcal{F} = \mathcal{F}_{\text{id}} + \mathcal{F}_{\text{exc}} \quad (5)$$

into an ideal gas contribution $\mathcal{F}_{\text{id}}$ and an unknown excess functional $\mathcal{F}_{\text{exc}}$ accounting for further interactions not present in an ideal gas.

External potentials are ignored in this study but can be easily added using the methods presented later. In Eq. (4), λ^3 denotes the thermal de Broglie wavelength (which is required here only for dimensional reasons), k_B is the Boltzmann constant, and T is the temperature. For the excess functional, there are multiple commonly used approximations such as fundamental measure theory (FMT) [75], the Ramakrishnan-Yussouff functional [76], or the Onsager functional [77] for liquid crystals.

B. Dynamical density functional theory

A widely used generalization of DFT is called dynamical density functional theory (DDFT) and is used to describe the dynamics of many-particle systems as a field theory of the one-particle density. An extensive review can be found in Ref. [38]. DDFT is, unlike DFT, not even in principle an exact theory, since it relies on the so-called adiabatic approximation, which assumes that a certain equilibrium relation, the Yvon-Born-Green relation (YBG-relation) [78], is valid in nonequilibrium [79], which is not the case. However, such a relation is approximately true for many systems not far from equilibrium. Again, more details on the derivation are given in Ref. [38].

The DDFT equation for biaxial particles has, as shown in Ref. [46], the general form

$$\partial_t \rho(\mathcal{R}, t) = \beta \nabla_{\mathcal{R}} \cdot \left(D(\mathcal{R}) \cdot \left(\rho(\mathcal{R}, t) \nabla_{\mathcal{R}} \frac{\delta \mathcal{F}[\rho(\mathcal{R}, t)]}{\delta \rho(\mathcal{R}, t)} \right) \right). \quad (6)$$

Here $\mathcal{R}$ denotes the vector $(\mathbf{R}, \mathbf{O})^T$ consisting of the spatial coordinate $\mathbf{R}$ and the angular orientation given by the three Euler angles $\mathbf{O} = (\phi, \theta, \chi)^T$. The diffusion tensor D is given by

$$D(\mathbf{O}) = \begin{pmatrix} D_{\text{TT}}(\mathbf{O}) & D_{\text{TR}}(\mathbf{O}) \\ D_{\text{RT}}(\mathbf{O}) & D_{\text{RR}}(\mathbf{O}) \end{pmatrix}, \quad (7)$$

where D_{TT} is the translational diffusion tensor, D_{RR} the rotational diffusion tensor, and D_{RT} and D_{TR} are tensors coupling translational and rotational diffusion. The spatial dependency of the diffusion coefficients might have in more complex cases is here ignored. Each of those matrices has three rows and columns (for three spatial coordinates and three Euler angles). The differential operator $\nabla_{\mathcal{R}} = (\nabla, \nabla_{\mathbf{O}})^T$ is a six-dimensional operator which contains in addition to the spatial

derivative ∇ the angular derivative operator $\nabla_{\mathbf{O}}$ with components

$$\begin{aligned}(\nabla_{\mathbf{O}})_1 &= -\cos(\phi) \cot(\theta) \partial_\phi - \sin(\phi) \partial_\theta - \cos(\phi) \csc(\theta) \partial_\chi, \\(\nabla_{\mathbf{O}})_2 &= -\sin(\phi) \cot(\theta) \partial_\phi + \cos(\phi) \partial_\theta + \sin(\phi) \csc(\theta) \partial_\chi, \\(\nabla_{\mathbf{O}})_3 &= \partial_\phi.\end{aligned}\quad (8)$$

C. Phase field crystal models

Equation (6) is, while being very general, also very complicated—it describes the dynamics of a density ρ defined on a six-dimensional configuration space, involves a 6×6 diffusion tensor leading to couplings between spatial and orientational derivatives, and is (due to the sometimes complicated form of DFT free-energy functionals) in general nonlocal. Therefore, practical applications require the development of a simpler model. Such a simplification is commonly achieved using phase-field crystal models (PFC models) [53,54], which can be derived via a series of approximations from (D)DFT [38,57] (and which alternatively can be obtained from macroscopic symmetry arguments).

II. BIAxIAL ORDER PARAMETERS

A. Scalar biaxial order parameters

As a common first step in the derivation of PFC models, we need to find an approximate expression for the density based on the symmetries of the system. The systematic method for doing this is to take an appropriate biaxial expansion of the density and truncate it after the second order. Higher orders of the expansion are not taken into account. The expansion coefficients will be related to a set of biaxial order parameters defined later; however, the exact relationship depends, of course, on the expansion we choose. This relationship arises from the fact that the order parameters are mathematically simply the projection of the density on some angular function, which might be part of a complete orthogonal basis. Common expansions are the expansion in Wigner D matrices as defined in (23), which is the biaxial generalization of spherical harmonics and the Cartesian expansion whose second order is an expansion in the elements R_{ij} of the rotation matrix for three Euler angles [as defined in (14)] and its coefficients are the elements of the Saupe matrix (at least almost, see Ref. [80]).

However, this raises a question: How do we know which expansion coefficients of a general expansion can be relevant for biaxial phases or particles? The short answer is that our expansion relies on certain symmetry arguments, as a consequence of which some order parameters are automatically zero. This is not unlike the uniaxial nematic phase, where a transformation $\mathbf{l}_3 \rightarrow -\mathbf{l}_3$ of the director $\mathbf{l}_3$ needs to leave the system unchanged and thus does not allow polar order parameters of the first order of an angular expansion. The details on the required conditions for the order parameters S, U, P, F employed here to be the only relevant ones are discussed below; however, a derivation is found in Ref. [73].

We first consider the case of constant directors, in which we can restrict ourselves to scalar order parameters. In addition to the orientation-averaged density ψ_1 and the uniaxial nematic order parameter S familiar from previous work [59], we employ the additional order parameters U, P , and F that

we have already used in Ref. [31] to study the equilibrium case. These order parameters are defined as

$$Y = \frac{5}{8\pi^2 \rho_0} \int d\mathbf{O} (\rho(\mathbf{O}, \mathbf{R}) - \rho_0) f_Y(\mathbf{O}), \quad (9)$$

$$\psi_1 = \frac{1}{8\pi^2 \rho_0} \int d\mathbf{O} (\rho(\mathbf{O}, \mathbf{R}) - \rho_0), \quad (10)$$

with $Y \in S, U, P, F$ and the functions

$$\begin{aligned}f_S(\mathbf{O}) &= \frac{3}{2} \cos^2(\theta) - \frac{1}{2}, \\f_U(\mathbf{O}) &= \frac{\sqrt{3}}{2} \sin^2(\theta) \cos(2\chi), \\f_P(\mathbf{O}) &= \frac{\sqrt{3}}{2} \sin^2(\theta) \cos(2\phi), \\f_F(\mathbf{O}) &= \frac{1}{2} (1 + \cos^2(\theta)) \cos(2\phi) \cos(2\chi) \\&\quad - \cos(\theta) \sin(2\phi) \sin(2\chi).\end{aligned}\quad (11)$$

Here ρ_0 denotes the constant bulk density (which could also be interpreted as a spatial and orientational average over $\rho(\mathbf{R}, \mathbf{O})$). A more detailed discussion of the physical meaning of the order parameters will be provided in Sec. III D. In the literature, there are different conventions for defining the order parameters. We here use a similar convention to the one employed in Ref. [61]; other works [31,73] omit the prefactor 5 in Eq. (10). [For the difference regarding Ref. [61], see the discussion under (36).] Of course, the definitions are equivalent, if used consistently. Note that we implicitly assume that there are no polar phases, as we would otherwise need to incorporate polar order parameters.

B. Tensorial biaxial order parameters

A further important aspect to take into account is the spatial dependence of the nematic directors, which would be relevant for instance when describing a nematic twist-bend phase. We therefore will now introduce general order parameters for a system with spatially varying nematic directors.

We begin by introducing the orthonormal tripods $\mathbf{m}_1, \mathbf{m}_2, \mathbf{m}_3$, constituting the basis of the molecular frame, $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$, constituting the basis of the fixed laboratory frame, and $\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3$, consisting of the three nematic directors, which we here explicitly allow to change over time and in space. Note that in uniaxial phases the nematic directors $\mathbf{l}_1$ and $\mathbf{l}_2$ are irrelevant, as there is ordering around only one axis, in which case the other nematic directors can be chosen arbitrarily. Finally, the molecular frame is particle fixed in the sense that the orientation of a particle is constant in this frame. It can be written through the projection on the laboratory frame:

$$\begin{aligned}\mathbf{m}_1 &= (\mathbf{m}_1 \cdot \mathbf{e}_1) \mathbf{e}_1 + (\mathbf{m}_1 \cdot \mathbf{e}_2) \mathbf{e}_2 + (\mathbf{m}_1 \cdot \mathbf{e}_3) \mathbf{e}_3, \\ \mathbf{m}_2 &= (\mathbf{m}_2 \cdot \mathbf{e}_1) \mathbf{e}_1 + (\mathbf{m}_2 \cdot \mathbf{e}_2) \mathbf{e}_2 + (\mathbf{m}_2 \cdot \mathbf{e}_3) \mathbf{e}_3, \\ \mathbf{m}_3 &= (\mathbf{m}_3 \cdot \mathbf{e}_1) \mathbf{e}_1 + (\mathbf{m}_3 \cdot \mathbf{e}_2) \mathbf{e}_2 + (\mathbf{m}_3 \cdot \mathbf{e}_3) \mathbf{e}_3.\end{aligned}\quad (12)$$

The projection of $\mathbf{m}_i$ on $\mathbf{e}_j$ is related to a rotation by

$$\mathbf{m}_i \cdot \mathbf{e}_j = R_{ji}, \quad (13)$$

while the elements R_{ji} of the corresponding rotation matrix are given by

$$\begin{aligned}
 R_{11} &= \cos(\phi) \cos(\theta) \cos(\chi) - \sin(\phi) \sin(\chi), \\
 R_{12} &= -\cos(\chi) \sin(\phi) - \cos(\phi) \cos(\theta) \sin(\chi), \\
 R_{13} &= \cos(\phi) \sin(\theta), \\
 R_{21} &= \cos(\phi) \sin(\chi) + \cos(\theta) \cos(\chi) \sin(\phi), \\
 R_{22} &= \cos(\phi) \cos(\chi) - \cos(\theta) \sin(\phi) \sin(\chi), \\
 R_{23} &= \sin(\phi) \sin(\theta), \\
 R_{31} &= -\cos(\chi) \sin(\theta), \\
 R_{32} &= \sin(\theta) \sin(\chi), \\
 R_{33} &= \cos(\theta).
 \end{aligned} \tag{14}$$

Now we will move on by constructing the tensors

$$\begin{aligned}
 \mathbf{M}_0 &= \sqrt{\frac{3}{2}} \left(\mathbf{m}_3 \otimes \mathbf{m}_3 - \frac{1}{3} \mathbf{I} \right), \\
 \mathbf{M}_1 &= \sqrt{\frac{1}{2}} (\mathbf{m}_1 \otimes \mathbf{m}_1 - \mathbf{m}_2 \otimes \mathbf{m}_2),
 \end{aligned} \tag{15}$$

and

$$\begin{aligned}
 \mathbf{L}_0 &= \sqrt{\frac{3}{2}} \left(\mathbf{l}_3 \otimes \mathbf{l}_3 - \frac{1}{3} \mathbf{I} \right), \\
 \mathbf{L}_1 &= \sqrt{\frac{1}{2}} (\mathbf{l}_1 \otimes \mathbf{l}_1 - \mathbf{l}_2 \otimes \mathbf{l}_2).
 \end{aligned} \tag{16}$$

Here $\mathbf{I}$ denotes the identity matrix in three dimensions and $\otimes$ denotes the Kronecker product (also known as the tensor product). The molecular tensors $\mathbf{M}_0$ and $\mathbf{M}_1$ are later averaged to become our tensor order parameters $\langle \mathbf{M}_0 \rangle$ and $\langle \mathbf{M}_1 \rangle$ and the tensors $\mathbf{L}_0$ and $\mathbf{L}_1$ will serve as a basis for an expansion of the tensor order parameters. Note that the relations presented here are not valid for any kind of biaxial particle (or biaxial phase). The assumption made here is that the particle (or more accurately, its pair interaction potential) needs to possess a D_{2h} symmetry. Informally, this corresponds to a “vertical flip-over” symmetry. It can be argued, as done in Ref. [31], that the results extend to certain other particles with different symmetry groups as well, since certain order parameters might be theoretically allowed but not necessarily physically relevant. However, generally speaking, other order parameters could arise via other symmetry groups. One example would be a particle shape like a prism or a pyramid that would destroy the $\mathbf{l}_3 \rightarrow -\mathbf{l}_3$ symmetry. In this case, (first-order) polar order parameters would arise and potentially be physically relevant. As another example, it might be of interest to study chiral particles or phases, which lack mirror symmetry. With this weaker symmetry assumption, there would be other second-order order parameters relevant. More discussion on this is given in Ref. [73].

As we will note soon, the density can be fully expressed using only the biaxial tensors presented above. First, we obtain the following expression for the averaged molecular tensors $\langle \mathbf{M}_0 \rangle$ and $\langle \mathbf{M}_1 \rangle$ by projecting them onto $\mathbf{L}_0$ and $\mathbf{L}_1$:

$$\begin{aligned}
 \langle \mathbf{M}_0 \rangle &= S \mathbf{L}_0 + P \mathbf{L}_1, \\
 \langle \mathbf{M}_1 \rangle &= U \mathbf{L}_0 + F \mathbf{L}_1,
 \end{aligned} \tag{17}$$

where we defined the S, U, P, F scalar order parameters as

$$\begin{aligned}
 S &= \langle \mathbf{M}_0 : \mathbf{L}_0 \rangle, \\
 U &= \langle \mathbf{M}_1 : \mathbf{L}_0 \rangle, \\
 P &= \langle \mathbf{M}_0 : \mathbf{L}_1 \rangle, \\
 F &= \langle \mathbf{M}_1 : \mathbf{L}_1 \rangle,
 \end{aligned} \tag{18}$$

and $\langle \cdots \rangle = \frac{5}{8\pi^2} \int d\mathbf{O} (\rho(\mathbf{R}, \mathbf{O}) - \rho_0) / \rho_0 \cdot (\cdots)$. A discussion of their physical significance is given in Sec. III D. The inner product : between two tensors $\mathbf{A}$ and $\mathbf{B}$

$$\mathbf{A} : \mathbf{B} = \text{Tr}(\mathbf{A}\mathbf{B}^T) \tag{19}$$

and the averaged molecular tensors $\langle \mathbf{M}_0 \rangle$ and $\langle \mathbf{M}_1 \rangle$ are

$$\begin{aligned}
 \langle \mathbf{M}_0 \rangle &= \frac{5}{8\pi^2 \rho_0} \int d\mathbf{O} (\rho(\mathbf{R}, \mathbf{O}) - \rho_0) \sqrt{\frac{3}{2}} \left(\mathbf{m}_3 \otimes \mathbf{m}_3 - \frac{1}{3} \mathbf{I} \right), \\
 \langle \mathbf{M}_1 \rangle &= \frac{5}{8\pi^2 \rho_0} \int d\mathbf{O} (\rho(\mathbf{R}, \mathbf{O}) - \rho_0) \\
 &\quad \times \sqrt{\frac{1}{2}} (\mathbf{m}_2 \otimes \mathbf{m}_2 - \mathbf{m}_1 \otimes \mathbf{m}_1).
 \end{aligned} \tag{20}$$

Apart from the microscopic definitions of $\langle \mathbf{M}_0 \rangle$ and $\langle \mathbf{M}_1 \rangle$ presented above, we note that, as commonly done in literature, the directors $\mathbf{l}_i$ and the scalar order parameters can be gained from the molecular tensors as their eigenvectors and eigenvalues, respectively. It is now easy to see that for a constant nematic director $\mathbf{l}_3 = (0, 0, 1)^T$ this more general approach coincides with the previous definition in (11). Now, generalizing some of the ideas outlined in Refs. [73] and [81], we express the biaxial density through the order parameters presented here by using orientational expansions. Although similar expressions appear in the earlier literature [81], previous work usually considered the case of constant directors (i.e., $\mathbf{l}_i$ coincides with $\mathbf{e}_i$), while we will later introduce a model for which we drop this requirement to find novel expressions for the description of biaxial phases.

III. DENSITY EXPANSIONS

A. Fixed directors

Now, having outlined the general theory for biaxial order, we want to apply this to our specific goal, namely the microscopic derivation of a field theory for biaxial liquid crystals. In order to do so, we first need to find an expansion of the one-particle density in terms of the order parameters introduced earlier. This will later, as outlined in Sec. IV B, allow us to gain closed-form expressions for the free energy in dependence of these order parameters.

One possibility for an orientational expansion of the one-particle density is to perform an expansion in elements of the rotation matrix R_{ij} , also known as the Cartesian expansion. The R_{ij} are given in Eq. (14). We give the explicit form for a generic function f up to second order here, and more details can be found in Refs. [80,82]:

$$f(\mathbf{R}, \mathbf{O}) = \psi(\mathbf{R}) + \sum_{i,j=1}^3 P_{ij}(\mathbf{R}) R_{ij} + \sum_{i,j,k,l=1}^3 Q_{ijkl} R_{ij} R_{kl}. \tag{21}$$

with the orientation-averaged density ψ , the polarization P_{ij} , and the generalized nematic tensor Q_{ijkl} , which here (unlike in the uniaxial case) are a second- and a fourth-rank tensors, respectively. They are given by

$$\begin{aligned}\psi &= \frac{1}{8\pi^2} \int d\mathbf{O} f(\mathbf{R}, \mathbf{O}), \\ P_{ij} &= \frac{3}{8\pi^2} \int d\mathbf{O} f(\mathbf{R}, \mathbf{O}) R_{ij}, \\ Q_{ijkl} &= \frac{5}{16\pi^2} \int d\mathbf{O} f(\mathbf{R}, \mathbf{O}) \left(R_{ij}R_{kl} + R_{il}R_{kj} - \frac{2}{3}\delta_{ik}\delta_{jl} \right).\end{aligned}\quad (22)$$

This expansion is closely related to the Saupe matrix [80], which is widely used in experiments [83].

Another widely used approach for a biaxial expansion of the density is the expansion in Wigner D matrices, also known as the angular multipole expansion, since it is the biaxial generalization of an expansion in spherical harmonics [82]. The Wigner D matrices D_{mn}^l are defined as [84]

$$D_{mn}^l = e^{-im\phi} e^{-in\chi} d_{mn}^l(\theta), \quad (23)$$

where d_{mn}^l is defined as

$$\begin{aligned}d_{mn}^l(\theta) &= \sqrt{(l+n)!(l-n)!(l+m)!(l-m)!} \\ &\times \sum_{k \in I_{mn}^l} \frac{(-1)^k \sin^{2l+m-n-2k}(\frac{\theta}{2}) \cos^{2k-m+n}(\frac{\theta}{2})}{(l+m-k)!(l-n-k)!k!(k-m+n)!}.\end{aligned}\quad (24)$$

Here I_{mn}^l is the set of all integers for which the arguments of the factorials appearing inside the sum in (24) are greater or equal to zero. This special case of an expansion in spherical harmonics has been used multiple times in the literature before, such as in Refs. [59,85].

Expressing the scalar order parameters S, U, P, F , discussed in Sec. II, in terms of Wigner D matrices results in

$$\begin{aligned}S &= \langle D_{00}^2 \rangle, \\ U &= \left\langle \frac{D_{02}^2 + D_{0-2}^2}{\sqrt{2}} \right\rangle, \\ P &= \left\langle \frac{D_{20}^2 + D_{-20}^2}{\sqrt{2}} \right\rangle, \\ F &= \left\langle \frac{D_{22}^2 + D_{-22}^2 + D_{2-2}^2 + D_{-2-2}^2}{2} \right\rangle,\end{aligned}\quad (25)$$

where $\langle \dots \rangle$ denotes the orientation average $\frac{5}{8\pi^2} \int d\mathbf{O} (\rho - \rho_0)/\rho_0$. These expressions can be derived from the definitions of f_S, f_F, f_P , and f_F provided in Ref. [86]. These relations will prove to be helpful in the expansion of the direct correlation function later.

For the density we pursue another approach, as the relation between the order parameters and the resulting expansion coefficients is still quite complicated for Wigner D matrices (which is similarly true for an expansion in rotation matrix

elements). We proceed by making the ansatz

$$\begin{aligned}\rho(\mathbf{R}, \mathbf{O}) &= \rho_0(1 + \psi_1 + S f_S(\mathbf{O}) + U f_U(\mathbf{O}) \\ &\quad + P f_P(\mathbf{O}) + F f_F(\mathbf{O}))\end{aligned}\quad (26)$$

for the density as a function of the scalar order parameters. We now give the explicit justification of this approximation for the density by doing an expansion to the second order in a set of matrices introduced by Mulder [86], which we will refer to as “Mulder matrices.” The expansion is not done directly in ρ but rather in $(\rho - \rho_0)/\rho_0$.

The Mulder matrices are an orthogonal function system and thus an orthogonal basis for a function f (which in our case is given by $(\rho - \rho_0)/\rho_0$), defined by the relation

$$\Delta_{mn}^l = \left(\frac{1}{\sqrt{2}} \right)^{2+\delta_{m0}+\delta_{n0}} \sum D_{\sigma m, \sigma_2 n}^l, \quad (27)$$

where the sum is such that $\sigma, \sigma_2 = -1, 1$; further, $0 \leq m, n \leq l$, and l, n, m are even [86]. They obey the orthogonality relations

$$\int_{\text{SO}(3)} d\mathbf{O} \Delta_{m_1 n_1}^{l_1} \Delta_{m_2 n_2}^{l_2} = \frac{8\pi^2}{2l+1} \delta_{l_1 l_2} \delta_{m_1 m_2} \delta_{n_1 n_2}. \quad (28)$$

Here the D_{mn}^l are the Wigner D matrices defined above.

The resulting expansion of an arbitrary function f into Mulder matrices is then given by

$$\begin{aligned}f(\mathbf{R}_1, \mathbf{R}_2, \mathbf{O}_1, \mathbf{O}_2) &= \sum_{j=1,2} \sum_{l_j, m_j, n_j} f_{l_j m_j n_j} \frac{(2l_1+1)(2l_2+1)}{64\pi^4} \Delta_{m_1 n_1}^{l_1} \Delta_{m_2 n_2}^{l_2},\end{aligned}\quad (29)$$

with

$$f_{l_1 m_1 n_1 l_2 m_2 n_2} = \int d\mathbf{O}_1 \int d\mathbf{O}_2 \Delta_{m_1 n_1}^{l_1} \Delta_{m_2 n_2}^{l_2} f(\mathbf{O}_1, \mathbf{O}_2, \mathbf{R}_1, \mathbf{R}_2). \quad (30)$$

[The orientational expansion of the density depends only on a single orientation $\mathbf{O}$, yet other expansions later will use a modified version of the general form in (29).]

After truncating the expansion in (29) at order $l = 2$, we need to define our order parameters as averages of the Mulder matrices. Since we know that only the averages of the f_Y and the orientational average of 1 (leading to the ψ_1 parameter) are relevant for the biaxial nematic phase, we need to find a way to express these averages through Mulder matrices. This can be achieved using the relations

$$\begin{aligned}\psi_1 &= \frac{1}{8\pi^2} \langle 1 \rangle = \frac{1}{8\pi^2} \langle \Delta_{00}^0 \rangle, \\ S &= \frac{5}{8\pi^2} \left\langle \frac{3}{2} \cos^2(\theta) - \frac{1}{2} \right\rangle = \frac{5}{8\pi^2} \langle \Delta_{00}^2 \rangle, \\ U &= \frac{5}{8\pi^2} \left\langle \frac{\sqrt{3}}{2} \sin^2(\theta) \cos(2\chi) \right\rangle = \frac{5}{8\pi^2} \langle \Delta_{02}^2 \rangle, \\ P &= \frac{5}{8\pi^2} \left\langle \frac{\sqrt{3}}{2} \sin^2(\theta) \cos(2\phi) \right\rangle = \frac{5}{8\pi^2} \langle \Delta_{20}^2 \rangle,\end{aligned}$$

$$F = \frac{5}{8\pi^2} \left\langle \frac{1}{2} (1 + \cos^2(\theta)) \cos(2\phi) \cos(2\chi) - \cos(\theta) \sin(2\phi) \sin(2\chi) \right\rangle = \frac{5}{8\pi^2} \langle \Delta_{22}^2 \rangle, \quad (31)$$

which, paired with (28), implies

$$\rho \approx \rho_0 \left(1 + \frac{\Delta_{00}^0}{8\pi^2} \langle \Delta_{00}^0 \rangle + \frac{5\langle \Delta_{00}^2 \rangle}{8\pi^2} \Delta_{00}^2 + \frac{5\langle \Delta_{02}^2 \rangle}{8\pi^2} \Delta_{02}^2 + \frac{5\langle \Delta_{20}^2 \rangle}{8\pi^2} \Delta_{20}^2 + \frac{5\langle \Delta_{22}^2 \rangle}{8\pi^2} \Delta_{22}^2 \right). \quad (32)$$

Alternatively, we can explicitly convert back to the S, U, P, F, ψ_1 parameters and arrive back at (26). [Note that (31) clarifies how we can formally define $f_{\psi_1} := 1$. The absence of a factor of 5 comes from the fact that the order parameters S, U, P, F appear in the second order of the orientational expansion, while ψ_1 comes from the zeroth order of the orientational expansion.]

B. Spatially varying directors

We now generalize the expansion Eq. (26) for spatially varying directors. In order to do so, we expand in the elements of the two tensors $\mathbf{M}_0$ and $\mathbf{M}_1$, as their averages fully characterize the system. The case for constant directors is presented in Ref. [81], and thus it is easy to see how the more general method presented here reduces to the previous known

case. Explicitly, the density can be written as

$$\begin{aligned} \rho &= \rho_0 (1 + \psi_1 + \langle \mathbf{M}_0 \rangle : \mathbf{M}_0 + \langle \mathbf{M}_1 \rangle : \mathbf{M}_1) \\ &= \rho_0 (1 + \psi_1 + (\langle \mathbf{M}_0 : \mathbf{L}_0 \rangle \mathbf{L}_0 + \langle \mathbf{M}_0 : \mathbf{L}_1 \rangle \mathbf{L}_1) : \mathbf{M}_0 \\ &\quad + (\langle \mathbf{M}_1 : \mathbf{L}_0 \rangle \mathbf{L}_0 + \langle \mathbf{M}_1 : \mathbf{L}_1 \rangle \mathbf{L}_1) : \mathbf{M}_1) \\ &= \rho_0 (1 + \psi_1 + \langle \mathbf{M}_0 : \mathbf{L}_0 \rangle \mathbf{M}_0 : \mathbf{L}_0 + \langle \mathbf{M}_0 : \mathbf{L}_1 \rangle \mathbf{M}_0 : \mathbf{L}_1 \\ &\quad + \langle \mathbf{M}_1 : \mathbf{L}_0 \rangle \mathbf{M}_1 : \mathbf{L}_0 + \langle \mathbf{M}_1 : \mathbf{L}_1 \rangle \mathbf{M}_1 : \mathbf{L}_1) \\ &= \rho_0 (1 + \psi_1 + S \mathbf{M}_0 : \mathbf{L}_0 + U \mathbf{M}_1 : \mathbf{L}_0 + P \mathbf{M}_0 : \mathbf{L}_1 \\ &\quad + F \mathbf{M}_1 : \mathbf{L}_1), \end{aligned} \quad (33)$$

which generalizes Eq. (32). Here $\langle \mathbf{M}_0 \rangle$ is (up to a conventional prefactor $\sqrt{3/2}$) the well-known nematic tensor $\mathbf{Q}$ also appearing, for instance, in the phenomenological Landau–de Gennes expansion of the free energy [87]. $\langle \mathbf{M}_1 \rangle$ is a similar tensor relevant for particles that are biaxial. (Notice that there can also be biaxial phases in a system of uniaxial particles, these correspond to a nonzero value of the order parameter P .)

C. Relation to expansions for uniaxial particles

Next, we show that our biaxial expansion reduces to the uniaxial one employed in previous work [59]. The first step is to neglect the order parameters U, P , and F . Then, assuming $P = U = F = 0$, the density from Eq. (33) has the form:

$$\rho = \rho_0 (1 + \psi_1 + S \mathbf{M}_0 : \mathbf{L}_0). \quad (34)$$

The expression appearing in the last term reads

$$\begin{aligned} \mathbf{M}_0 : \mathbf{L}_0 &= \frac{3}{2} \left((\mathbf{m}_3 \cdot \mathbf{e}_j)(\mathbf{m}_3 \cdot \mathbf{e}_i)(\mathbf{l}_3 \cdot \mathbf{e}_j)(\mathbf{l}_3 \cdot \mathbf{e}_i) - \frac{3}{9} - \frac{(\mathbf{m}_3 \cdot \mathbf{e}_j)(\mathbf{m}_3 \cdot \mathbf{e}_i)(\mathbf{e}_i \cdot \mathbf{e}_j) + (\mathbf{l}_3 \cdot \mathbf{e}_j)(\mathbf{l}_3 \cdot \mathbf{e}_i)(\mathbf{e}_i \cdot \mathbf{e}_j)}{3} \right) \\ &= \frac{3}{2} \left((\mathbf{m}_3 \cdot \mathbf{l}_3)^2 - \frac{2}{3} + \frac{1}{9} (\mathbf{e}_i \cdot \mathbf{e}_i)(\mathbf{e}_j \cdot \mathbf{e}_j) \right) = \frac{3}{2} \left((\mathbf{m}_3 \cdot \mathbf{l}_3)^2 - \frac{1}{3} \right) = L_2(\mathbf{m}_3 \cdot \mathbf{l}_3), \end{aligned} \quad (35)$$

where L_2 is the second Legendre polynomial. This agrees with the result by Wittkowski *et al.* [59] (their $\hat{u}_0$ corresponds to our $\mathbf{l}_3$ and our $\mathbf{m}_3$ corresponds to their $\hat{u}$):

$$\rho = \rho_0 (1 + \psi_1 + S L_2(\mathbf{m}_3 \cdot \mathbf{l}_3)). \quad (36)$$

(Somewhat more subtle, our density still has a χ dependence, as seen by the remaining normalization factor proportional to $1/(8\pi^2)$, since we still integrate over all three Euler angles. However, the density distribution for χ is uniform, as we assumed $U = P = F = 0$, and thus absorbed in the different prefactors for the order parameters as compared to Refs. [59] and [61], where the χ dependence was neglected entirely.) Our method thus generalizes the results of Ref. [59] to both biaxial particles and biaxial phases. In the literature one can find many more applications than derivation of PFC models with such expansions; they have, for example recently also found application in machine learning for liquid crystals [88].

D. Meaning of the scalar order parameters

Analogously to (35), we recover the definitions in terms of $\mathbf{m}_i$ and $\mathbf{l}_i$ for S, P, U , and F as given in Ref. [73]:

$$\begin{aligned} S &= \frac{3}{2} \left\langle \left(\mathbf{m}_3 \cdot \mathbf{l}_3 - \frac{1}{3} \right) \right\rangle, \\ U &= \frac{\sqrt{3}}{2} \langle (\mathbf{m}_1 \cdot \mathbf{l}_3)^2 - (\mathbf{m}_2 \cdot \mathbf{l}_3)^2 \rangle, \\ P &= \frac{\sqrt{3}}{2} \langle (\mathbf{m}_3 \cdot \mathbf{l}_1)^2 - (\mathbf{m}_3 \cdot \mathbf{l}_2)^2 \rangle, \\ F &= \frac{1}{2} \langle (\mathbf{m}_1 \cdot \mathbf{l}_1)^2 - (\mathbf{m}_1 \cdot \mathbf{l}_2)^2 - (\mathbf{m}_2 \cdot \mathbf{l}_1)^2 + (\mathbf{m}_2 \cdot \mathbf{l}_2)^2 \rangle, \end{aligned} \quad (37)$$

where the directors are now, in contrast to Ref. [73], explicitly space and time dependent. This notation also helps us to develop some intuition for the physical meaning of the order parameters introduced here:

(i) S : order parameter for uniaxiality: This order parameter measures the alignment of the molecular axis $\mathbf{m}_3$ with the the director $\mathbf{l}_3$ (often referred to as *the* nematic director). It is 0 in an isotropic phase and 1 in the perfectly nematic phase.

(ii) U : order parameter for *molecular* biaxiality: This order parameter is nonzero only if the particle shape is biaxial. However, U can be nonzero even in a phase which is not biaxial. This can be understood by recognizing that the uniaxial (molecular) symmetry transformation $\mathbf{m}_1 \rightarrow -\mathbf{m}_1, \mathbf{m}_2 \rightarrow -\mathbf{m}_2$ does not leave the order parameter invariant, but the uniaxial (phase) symmetry transformation $\mathbf{l}_1 \rightarrow -\mathbf{l}_1, \mathbf{l}_2 \rightarrow -\mathbf{l}_2$ does leave the order parameter invariant, as expected.

(iii) P : order parameter for *phase* biaxiality: Here the uniaxial phase symmetry transformation $\mathbf{l}_1 \rightarrow -\mathbf{l}_1, \mathbf{l}_2 \rightarrow -\mathbf{l}_2$ does not leave P invariant; however, assuming uniaxial symmetry in the shape through $\mathbf{m}_1 \rightarrow -\mathbf{m}_1, \mathbf{m}_2 \rightarrow -\mathbf{m}_2$ leaves the order parameter invariant. As a result, this order parameter accounts for biaxiality in the phase. This means, this order parameter can be nonzero for both uniaxial and biaxial particle shapes, but it can only be nonzero in a biaxial phase.

(iv) F : order parameter for *full* biaxiality: This order parameter is only nonzero if both the particle shape and the phase are biaxial. Uniaxial symmetry transformations of the molecular axes or the director axes both do not leave the order parameter invariant. Thus, it can only be nonzero for full biaxiality.

Note that there is, as noted earlier already, in general a difference between *biaxial phases* and *biaxial particles*. A biaxial phase is a phase in which, in addition to S , P is also nonzero—which can at least mathematically also happen if the underlying particles are uniaxial. In contrast, U and F can only be nonzero if the particles are biaxial (an example for this would be hard cuboids).

Finally, we note that we can recover the special case for constant directors discussed in Sec. III A by simply setting $\mathbf{l}_i = \mathbf{e}_i$. Note that in this case the names “director frame” and “laboratory frame” can be and are used interchangeably [73,81]. This no longer holds in the general time-dependent case that we consider here.

IV. FREE ENERGIES

A. Macroscopic model

There have been multiple studies investigating the formulation of a macroscopic model incorporating full biaxiality by generalizing the early uniaxial macroscopic theory of de Gennes [1], such as done in, e.g., Refs. [89–93]. Here we give a short overview over these results. General methods for the derivation can be found in Refs. [93] and [92].

We formulate our theory with the tensors $\mathbf{Q} = \langle \mathbf{M}_0 \rangle$ and $\mathbf{K} = \langle \mathbf{M}_1 \rangle$. However, very often authors assume that $\mathbf{Q} = \sqrt{3/2} \langle \mathbf{M}_0 \rangle$ and $\mathbf{K} = \langle \mathbf{M}_1 \rangle / \sqrt{2}$ for their macroscopic models. This difference is solely notation convention and does not influence the physics. $\mathbf{Q}$ is often used for denoting the well-known nematic/uniaxial order tensor whose largest eigenvalue is equal to S , with the corresponding eigenvector being $\mathbf{l}_3$ [94]. (“Uniaxial” refers to particle uniaxiality here. $\mathbf{Q}$ is capable of describing phase biaxiality, for example the biaxial structure of the cores of topological defects and the intrinsic structure of the nematic-isotropic interface.) In a theory accounting for

the coupling of the two tensors $\mathbf{Q}$ and $\mathbf{K}$, the bulk energy is given by the following linear combination of tensor invariants up to fourth order where we combined expressions from Refs. [89,90] and Ref. [54] to arrive at the following expression for the free-energy density f :

$$\begin{aligned} f = & b_1 \text{Tr}(\mathbf{Q}^2) + b_2 \text{Tr}(\mathbf{Q}^3) + b_3 \text{Tr}(\mathbf{Q}^2)^2 + b_4 \text{Tr}(\mathbf{K}^2) \\ & + b_5 \text{Tr}(\mathbf{K}^2)^2 + b_6 \text{Tr}(\mathbf{Q}\mathbf{K})^2 + b_7 \text{Tr}(\mathbf{Q}^2\mathbf{K}^2) + b_8 \text{Tr}(\mathbf{Q}\mathbf{K}) \\ & + b_9 \text{Tr}(\mathbf{K}^3) + b_{10} \text{Tr}(\mathbf{Q}^2\mathbf{K}) + b_{11} \text{Tr}(\mathbf{Q}^3\mathbf{K}) \\ & + b_{12} \text{Tr}(\mathbf{Q}\mathbf{K}^3) + b_{13} \text{Tr}(\mathbf{K}^2) \text{Tr}(\mathbf{Q}^2) + b_{14} \psi_1^2 + b_{15} \psi_1^3 \\ & + b_{16} \psi_1^4 + b_{17} \psi_1 \text{Tr}(\mathbf{Q}\mathbf{K}) + b_{18} \psi_1 \text{Tr}(\mathbf{Q}^2) \\ & + b_{19} \psi_1 \text{Tr}(\mathbf{K}^2) + b_{20} \psi_1 \text{Tr}(\mathbf{Q}^3) + b_{21} \psi_1 \text{Tr}(\mathbf{K}^3) \\ & + b_{22} \psi_1 \text{Tr}(\mathbf{K}^2\mathbf{Q}) + b_{23} \psi_1 \text{Tr}(\mathbf{Q}^2\mathbf{K}) + b_{24} \psi_1^2 \text{Tr}(\mathbf{Q}^2) \\ & + b_{25} \psi_1^2 \text{Tr}(\mathbf{K}^2) + b_{26} \psi_1^2 \text{Tr}(\mathbf{Q}\mathbf{K}). \end{aligned} \quad (38)$$

The coefficients $b_1 - b_{26}$ are macroscopic parameters chosen in accordance with simulations or experimental data and Tr denotes the trace operator. Clearly, the expansion (38) is much more complicated than the uniaxial theory proposed by de Gennes, which is only based on $\mathbf{Q}$ [1]—in Eq. (38); we have a total of 26 independent terms. Now, following the notation introduced in Ref. [91], we include the elastic energy. For a tensor $\mathbf{A}$, we define gradient and divergence as

$$\begin{aligned} (\nabla \mathbf{A})_{i,j_1 \dots j_n} &= \partial_i \mathbf{A}_{j_1 \dots j_n}, \\ (\nabla \cdot \mathbf{A})_{j_1 \dots j_{n-1}} &= \sum_i \partial_i \mathbf{A}_{j_1 \dots j_{n-1}, i} \end{aligned} \quad (39)$$

and for two tensors $\mathbf{A}$ and $\mathbf{B}$ use the inner product : as defined in (19). In this notation, the form obtained by Xu and Chen [91] for the elastic free-energy density of a coupling of two distinct symmetric traceless tensors $\mathbf{Q}$ and $\mathbf{K}$ with each other and with a scalar field ψ is

$$\begin{aligned} f = & c_1 (\nabla \psi_1) : (\nabla \psi_1) + c_2 (\nabla \mathbf{Q}) : (\nabla \mathbf{Q}) + c_3 (\nabla \mathbf{Q}) : (\nabla \mathbf{K}) \\ & + c_4 (\nabla \mathbf{K}) : (\nabla \mathbf{K}) + c_5 (\nabla \cdot \mathbf{Q}) : (\nabla \cdot \mathbf{Q}) \\ & + c_6 (\nabla \cdot \mathbf{Q}) : (\nabla \cdot \mathbf{K}) + c_7 (\nabla \cdot \mathbf{K}) : (\nabla \cdot \mathbf{K}) \\ & + c_8 (\nabla \psi_1) : (\nabla \cdot \mathbf{K}) + c_9 (\nabla \psi_1) : (\nabla \cdot \mathbf{Q}) \\ & + c_{10} (\nabla^2 \psi_1) : (\nabla^2 \psi_1). \end{aligned} \quad (40)$$

Once again, the coefficients $c_1 - c_{10}$ are just macroscopic coefficients chosen in accordance with simulations or experimental data. We chose to include the term $c_{10} (\nabla^2 \psi_1) : (\nabla^2 \psi_1)$ despite the fact that we are only looking at contributions up to second order in gradients—the reason for that is that such a term allows for the formation of crystals. Note that Eq. (40) holds only for particles with symmetry group D_{2h} . Reference [91] only gives the bulk energy up to second order. Another theory is given in Ref. [89], where both the full elastic energy and the bulk energy up to fourth order is presented. However, unlike Ref. [91], Ref. [89] does not include the coupling of the space-dependent density with the nematic tensors.

B. General route to mesoscopic PFC models

We now present the general approach for systematic microscopic derivations of phase-field crystal models, which naturally account for, in principle, all couplings up to any order, following previous work on the subject [52,55–57]. We then use the presented ideas to derive two models for biaxial liquid crystals.

First, we consider the *ideal gas free energy*:

(1) We insert the parametrization (33) of the density in terms of the order parameters into the ideal gas free energy (4).

(2) We Taylor expand the logarithm in Eq. (4) up to third order (such that the resulting expression for $\mathcal{F}_{\text{id}}$ is a fourth-order polynomial). An expansion up to third order is common as it allows to model crystal formation [54].

(3) We evaluate the angular integrals.

For the *excess free energy*, the derivation is somewhat more complicated:

(1) We choose a suitable approximation for the excess free energy, the explicit form of which is not known. We will here work with the common Ramakrishnan-Yussouf approximation [76], where the excess free energy is written in terms of the second-order direct correlation function. Other approaches, such as a higher-order functional Taylor expansion, are also possible and have been investigated before [46,52,61].

(2) We insert the parametrization (33) of the density in terms of the order parameters into the excess free energy.

(3) Since the orientational dependence of the direct correlation function is generally unknown, we need to perform an orientational expansion respecting the internal symmetries of the system. Details are given later.

(4) We evaluate the angular integrals.

(5) The resulting expression involves a convolution integral. In order to remove this nonlocality, we perform a gradient expansion up to second order (fourth order for terms only involving ψ_1). This is a common choice in PFC modeling [52,54].

This is the basic procedure for deriving phase-field crystal models for liquid crystals. Of course, details may vary. In what follows, we show explicitly how to use this method for a microscopic derivation of the free energy of a model system. Specifically, we introduce a restricted model for full biaxiality (by fixing the directors) and a full model for phase biaxiality (by dropping order parameters related to particle biaxiality).

C. Overview over the considered models

In the following, we will obtain microscopic expressions for the coefficients of two different models:

(i) *Model 1* incorporates all five scalar order parameters, ψ_1 , S , U , P , and F , yet holds the directors constant, where we use the density expansion (26) instead of (33). This means it describes both biaxial phases and biaxial particles but does not incorporate elastic interactions, which are, for instance, responsible for the formation of twist-bend nematics.

(ii) *Model 2* incorporates the scalar order parameters ψ_1 , S , and P and does not hold the directors $\mathbf{l}_i$ constant, where we drop the other terms in the density expansion (33). As such, it fully incorporates the well-known tensor order parameter $\mathbf{Q}$ and its coupling with the orientation averaged density

ψ_1 . However, it is limited by not incorporating the second tensor order parameter $\mathbf{K}$ associated with the two scalar order parameters U and F and thus is not able to describe the effects induced by molecular biaxiality that would be captured by U and F .

It is important to note that both of these models are special cases of the more general macroscopic theory presented in Sec. IV A. The elastic energy in Eq. (40) provides a good example: If we restrict ourselves to the term $(\nabla \mathbf{Q}) \cdot (\nabla \mathbf{K})$ and assume the directors to be constant, as done in Model 1, then we arrive at $(\nabla S) \cdot (\nabla U) + (\nabla P) \cdot (\nabla F)$. In the case of neglecting shape biaxiality, though, we can easily recognize that this simply means $\mathbf{K} = 0$ and the term will thus vanish completely. In summary, each of our simplified models capture one aspect of the more general macroscopic model. However, while the macroscopic theory is the most general one of the models presented here, the microscopic derivation has the advantage of providing microscopic expressions for the coefficients and would, if carried out in full generality, reproduce the macroscopic model.

An explicit microscopic derivation of the full biaxial model would be practically difficult due to the high number of free parameters (see Sec. IV A) and the complex form of the density with a total of 10 independent tensor elements. However, after deriving the free energy for Model 1 in Sec. IV D, we develop a method to infer the full biaxial model from it in Sec. IV E, where we combine the microscopic result with the macroscopic model from Sec. IV A. Then, in Sec. IV F, we introduce and discuss an important special case of the full biaxial model presented in Sec. IV E (namely the case of uniaxial particle shapes). Later, in Sec. V, we only derive dynamic equations for the restricted Models 1 and 2 to avoid calculating a large number of integral necessary for dynamics.

D. Model 1

We first consider the case where, as in previous work [31], directors are held constant, implying that we have to deal with a density $\rho(\mathbf{O}, \psi_1, S, U, P, F)$. Explicitly, we assume the form presented in (26). Note that this considers both tensors $\langle \mathbf{M}_0 \rangle$ and $\langle \mathbf{M}_1 \rangle$ with constant directors $\mathbf{l}_i$. As an important fact, keep in mind that the exact form of $\mathbf{l}_i$ matters. Here we choose $\mathbf{l}_3 = (0, 0, 1)$, $\mathbf{l}_2 = (0, 1, 0)$. Other (constant) choices are possible but will alter both the density and the resulting free energy.

1. Ideal gas free energy

We begin with calculating the ideal gas free energy. As discussed above, we substitute $x = \frac{\rho - \rho_0}{\rho_0}$ using Eq. (33) and Taylor expand the logarithm to third order, resulting in

$$\begin{aligned} \beta \mathcal{F}_{\text{id}} &= \int d\mathbf{R} \int d\mathbf{O} \rho (\ln(\rho \lambda^3) - 1) \\ &= \rho_0 \int d\mathbf{R} \int d\mathbf{O} (1 + x) (\ln(\lambda^3 \rho_0 (1 + x)) - 1) \\ &\approx \mathcal{F}_0 + \rho_0 \int d\mathbf{R} \int d\mathbf{O} \left(\frac{x^2}{2} - \frac{x^3}{6} + \frac{x^4}{12} \right), \end{aligned} \quad (41)$$

where $\mathcal{F}_0$ consists of irrelevant constant terms the functional derivative of which vanishes. Now, we need to calculate the angular integrals by first inserting the density defined in

Eq. (26) into the expression Eq. (41) and then calculating integrals of the form $\int d\mathbf{O} f_Y(\mathbf{O})^a f_X(\mathbf{O})^b$ with a and b being integers obeying $a + b \leq 4$. For a or b equal to 1 or 0, we

can use the orthogonality relations (28), which, for example, imply that terms of the form $\int d\mathbf{O} f_S(\mathbf{O}) f_F(\mathbf{O})$ vanish. Otherwise, the integrals are calculated numerically. The result is

$$\begin{aligned} \beta \mathcal{F}_{\text{id}} = & \mathcal{F}_0 + 8\pi^2 \rho_0 \int d\mathbf{R} \left(\frac{1}{2} \left(\psi_1^2 + \sum_X \frac{X^2}{5} \right) - \frac{1}{6} \left(\psi_1^3 + \frac{3\psi_1}{5} \sum_X X^2 - \frac{2}{35} (3P^2S + 3U^2S - 3F^2S - 6UPF - S^3) \right) \right. \\ & + \frac{1}{12} \left(\psi_1^4 + \sum_X \frac{3X^4}{35} + \psi_1^2 \sum_X \frac{6X^2}{5} - \frac{2}{35} \psi_1 (12P^2S + 12U^2S - 12F^2S - 24UPF - 4S^3) \right. \\ & \left. \left. + \frac{1}{35} (12F^2S^2 + 6F^2U^2 + 6F^2P^2 + 6S^2P^2 + 6S^2U^2 + 12U^2P^2 - 12SUPF) \right) \right), \end{aligned} \quad (42)$$

where $\mathcal{F}_0$ is an irrelevant constant and $X \in \{S, U, P, F\}$.

2. Excess free energy

Now, we turn our attention towards $\mathcal{F}_{\text{exc}}$. We employ the widely used Ramakrishnan-Yussouff approximation [76],

$$\begin{aligned} \beta \mathcal{F}_{\text{exc}} = & \frac{1}{2} \int d\mathbf{R}_1 \int d\mathbf{R}_2 \int d\mathbf{O}_1 \int d\mathbf{O}_2 c^{(2)} \\ & \times (\mathbf{R}_1, \mathbf{R}_2, \mathbf{O}_1, \mathbf{O}_2) (\rho(\mathbf{R}_1, \mathbf{O}_1) - \rho_0) (\rho(\mathbf{R}_2, \mathbf{O}_2) - \rho_0), \end{aligned} \quad (43)$$

with the direct correlation function $c^{(2)}$ of the reference state ρ_0 that is defined as

$$\beta c^{(2)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{O}_1, \mathbf{O}_2) = \frac{-\delta^2 \mathcal{F}_{\text{exc}}}{\delta \rho_1(\mathbf{R}_1, \mathbf{O}_1) \delta \rho_2(\mathbf{R}_2, \mathbf{O}_2)} \Big|_{\rho=\rho_0}. \quad (44)$$

The definition (44) makes Eq. (43) a functional Taylor expansion of $\mathcal{F}_{\text{exc}}$, where we expand around a constant bulk density ρ_0 .

We can simplify $c^{(2)}$ by exploiting the symmetries that the system has in the state $\rho = \rho_0$ where it is evaluated. First, we employ spatial homogeneity, which implies that

$$c^{(2)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{O}_1, \mathbf{O}_2) = c^{(2)}(\mathbf{R}_1 + \mathbf{a}, \mathbf{R}_2 + \mathbf{a}, \mathbf{O}_1, \mathbf{O}_2) \quad (45)$$

with an arbitrary vector $\mathbf{a}$. Note that the assumption of spatial homogeneity of $c^{(2)}$, although frequently made, is not always true—it breaks down for example in crystals [since $c^{(2)}$ is a functional of the density which, in a crystal, is not homogeneous]. For details see Ref. [95], where this was recently investigated in greater detail. In our case, however, $c^{(2)}$ is homogeneous since we make an expansion around a spatially homogeneous isotropic equilibrium density ρ_0 .

Setting $\mathbf{a} = -\mathbf{R}_2$, it follows that

$$c^{(2)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{O}_1, \mathbf{O}_2) = c^{(2)}(\mathbf{R}_1 - \mathbf{R}_2, \mathbf{O}_1, \mathbf{O}_2). \quad (46)$$

Next, we exploit the fact that the system is spatially isotropic. Mathematically, this implies that it is invariant under a rotation $\mathbf{D}$, such that

$$c^{(2)}(\mathbf{R}_1 - \mathbf{R}_2, \mathbf{O}_1, \mathbf{O}_2) = c^{(2)}(\mathbf{D} \cdot (\mathbf{R}_1 - \mathbf{R}_2), \mathbf{D}\mathbf{O}_1, \mathbf{D}\mathbf{O}_2). \quad (47)$$

Note that $\mathbf{D}$ is an abstract rotation operator here, which does not have to be represented by the standard rotation matrix (as the

orientation $\mathbf{O}$ also is, since three Euler angles and thus three molecular axis are needed, not represented by a single vector). We choose $\mathbf{D}$ in such a way that $\mathbf{R}_1 - \mathbf{R}_2$ lies on the z axis:

$$\begin{aligned} c^{(2)}(\mathbf{D} \cdot (\mathbf{R}_1 - \mathbf{R}_2), \mathbf{D}\mathbf{O}_1, \mathbf{D}\mathbf{O}_2) \\ = c^{(2)}(|\mathbf{R}_1 - \mathbf{R}_2| \mathbf{e}_z, \mathbf{D}\mathbf{O}_1, \mathbf{D}\mathbf{O}_2), \end{aligned} \quad (48)$$

where $\mathbf{e}_z$ is the unit vector in z direction. Now we need to find a way to expand the direct correlation function in a way that allows us to evaluate the resulting angular integrals. We cannot choose a simple expansion in spherical harmonics as done in Ref. [59] since $c^{(2)}$ depends on three angles, such that an expansion in spherical harmonics is no longer sufficient. Further, we need to choose an expansion that respects the internal symmetries of the system, such as the one presented in Appendix A of Ref. [45] (where, however, the biaxial expansion coefficients are not given) and applied (for uniaxial systems only) in Refs. [59,96]. The chosen expansion for this purpose has (using the abbreviation $\mathbf{R} := \mathbf{R}_1 - \mathbf{R}_2$ and defining $\mathbf{O}_{12}$ as the orientation of $\mathbf{R} := \mathbf{R}_1 - \mathbf{R}_2$) the form

$$c^{(2)}(|\mathbf{R}| \mathbf{e}_z, \mathbf{O}_{12}, \mathbf{O}_1, \mathbf{O}_2) = \sum_{\lambda} \omega_{\lambda} (|\mathbf{R}| \mathbf{e}_z) \phi_{\lambda}(\mathbf{O}_{12}, \mathbf{O}_1, \mathbf{O}_2), \quad (49)$$

with the orientational part

$$\begin{aligned} \phi_{\lambda}(\mathbf{O}_{12}, \mathbf{O}_1, \mathbf{O}_2) = & \sum_{m_1, m_2, m} C(l_1, l_2, l, m_1, m_2, m) (D_{m_1 n_1}^{l_1})^* \\ & \times (\mathbf{O}_1) (D_{m_2 n_2}^{l_2})^* (\mathbf{O}_2) Y_{lm}^*(\mathbf{O}_{12}). \end{aligned} \quad (50)$$

Note that $\mathbf{O}_{12}$ only depends on two angles given in spherical coordinates, as it specifies the orientation between the two vectors $\mathbf{R}_1$ and $\mathbf{R}_2$ within center-of-mass coordinate. In contrast, $\mathbf{O}_1$ and $\mathbf{O}_2$ specify the orientation of a particle in terms of Euler angles and thus depend on three angles. We have used the multi-index $\lambda = (l_1, n_1, l_2, n_2, l)$ and the coefficients

$$\begin{aligned} \omega_{\lambda} = & \frac{(2l_1 + 1)(2l_2 + 1)}{64\pi^4} \sqrt{\frac{4\pi}{2l + 1}} \int d\mathbf{O}_1 \int d\mathbf{O}_2 \\ & \times \sum_{m=\min(l_1, l_2)}^{m=\max(l_1, l_2)} C(l_1, m, l_2, -m, l, 0) \\ & \times D_{m_1 n_1}^{l_1}(\mathbf{O}_1) D_{m_2 n_2}^{l_2}(\mathbf{O}_2) c^{(2)}(|\mathbf{R}| \mathbf{e}_z, \mathbf{O}_1, \mathbf{O}_2). \end{aligned} \quad (51)$$

The essential idea of this expansion is that both ϕ_λ and $c^{(2)}$ are invariant under a rotation of all angles. The $C(l_1, m_1, l_2, m_2, l, m)$ are the Clebsch-Gordan coefficients. This is sufficient for our next steps.

To obtain the excess free energy, we start by inserting Eqs. (49) and (32) into Eq. (43) and integrating out the orientational degrees of freedom. This gives

$$\begin{aligned} \mathcal{F}_{\text{exc}} = & \frac{1}{2} \int d\mathbf{R}_1 \int d\mathbf{R}_2 \sum_{X,Z,l} \frac{64\pi^4 \rho_0^2}{(2l_X + 1)(2l_Z + 1)} \\ & \times X(\mathbf{R}_1) Z(\mathbf{R}_2) \omega_{S(X)_1, S(X)_3, S(Z)_1, S(Z)_3, l}(\mathbf{R}_1 - \mathbf{R}_2) \\ & \times C(S(X)_1, S(X)_2, S(Z)_1, S(Z)_2, l, m_X + m_Z) \end{aligned} \quad (52)$$

with $X, Z \in \{\psi_1, S, U/\sqrt{2}, P/\sqrt{2}, F/2\}$ and $S(X) = (l_X, m_X, n_X)$

$$\begin{aligned} S(\psi_1) &= (0, 0, 0), \\ S(S) &= (2, 0, 0), \\ S(U) &= (2, 0, 2) \quad \text{or} \quad (2, 0, -2), \\ S(P) &= (2, 2, 0) \quad \text{or} \quad (2, -2, 0), \\ S(F) &= (2, 2, 2) \quad \text{or} \quad (2, -2, -2) \\ &\quad \text{or} \quad (2, -2, 2) \quad \text{or} \quad (2, 2, -2). \end{aligned} \quad (53)$$

The notation $\mathcal{S}(X)_i$ is to be understood such that it denotes the i th element of $\mathcal{S}(X)$ as given in (53). As an example, if we are interested in the terms coupling S and P , then the required Clebsch-Gordan coefficient would be either $C(2, 0, 2, 2, 2, 2)$ or $C(2, 0, 2, -2, 2, -2)$ (since P is expressed through a sum of two Wigner D matrices), and the factor ω_λ would be ω_{20202} (in both cases). Explicitly, $\mathcal{S}(X)_2$ would be either 2 or -2. Both combinations need to be realized such that a single order parameter might result in multiple terms. Note that $m = m_1 + m_2$, as otherwise the Clebsch-Gordan coefficient would be 0. Due to the gradient expansion we will perform later, $l \in 0, 2$, since the integral $\int d\mathbf{O} Y_{lm} \mathbf{m}_3 \otimes \mathbf{m}_3$ is nonvanishing only for $l \in 0, 2$. Thus, effectively, only the spherical harmonics Y_{00}, Y_{20}, Y_{22} , and Y_{2-2} are allowed. Afterwards, we perform a change of variables $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ and Taylor expand the order parameter $X(\mathbf{R}_2 + \mathbf{R})$ with respect to $\mathbf{R}$. (This last step is usually referred to as a “gradient expansion.”) For a generic function f , we can make the following expansion (which we will truncate at order $l = 2$ and order $l = 4$ for terms only involving ψ_1):

$$f(\mathbf{R} + \bar{\mathbf{R}}) = \sum_l \frac{\bar{R}^l}{l!} (\bar{\mathbf{u}} \cdot \nabla)^l f(\mathbf{R}), \quad (54)$$

with $\mathbf{R}, \bar{\mathbf{R}} = \bar{R}\bar{\mathbf{u}}$ being arbitrary vectors. Here $\bar{\mathbf{u}}$ is the unit vector with the same orientation as $\bar{\mathbf{R}}$, while $\bar{R}$ denotes the absolute value of $\bar{\mathbf{R}}$. Finally, we evaluate the integral over $\mathbf{R}$ and arrive at

$$\begin{aligned} \mathcal{F}_{\text{exc}} = & \frac{1}{2} \int d\mathbf{R}_1 \sum_{X,Z,l} \frac{64\pi^4 \rho_0^2 X(\mathbf{R}_1)}{(2l_X + 1)(2l_Z + 1)} C(S(X)_1, S(X)_2, S(Z)_1, S(Z)_2, l, m) \\ & \times \left(Z(\mathbf{R}_1) \left(\int d|\mathbf{R}| |\mathbf{R}|^2 \omega_{S(X)_1, S(X)_3, S(Z)_1, S(Z)_3, l}(|\mathbf{R}|\mathbf{e}_z) \int d\mathbf{O} Y_{lm} \right) \right. \\ & \left. + \sum_{i,j} \partial_i \partial_j Z(\mathbf{R}_1) \left(\int d|\mathbf{R}| \frac{|\mathbf{R}|^4}{2} \omega_{S(X)_1, S(X)_3, S(Z)_1, S(Z)_3, l}(|\mathbf{R}|\mathbf{e}_z) \int d\mathbf{O} Y_{lm} m_{3,i} m_{3,j} \right) \right) \end{aligned} \quad (55)$$

with the constraints on l, m , and S as explained above. The values of l_X, m_X, n_X and l_Z, m_Z, n_Z are connected to the sum over X, Z as given in (53). The integrals $\int_{S_2} d\mathbf{O} Y_{lm}$ and $\int_{S_2} d\mathbf{O} Y_{lm} m_{3,i} m_{3,j}$ are given in detail in Appendix A 1.

E. Inferring the full biaxial model

While an explicit derivation would be very tedious and practically very difficult, the coefficients of the (macroscopic) full biaxial model from Sec. IV A. can be microscopically determined by a comparison to the special (and much less complex) case of constant directors (Model 1), for which we provided an explicit microscopic derivation in Sec. IV D. This (quite surprising) result is obtained as follows: The key to establish a link between the corresponding free energies is the relation (17) of the averaged molecular tensors $\langle \mathbf{M}_0 \rangle$ and $\langle \mathbf{M}_1 \rangle$ to the scalar order parameters S, U, P, F . We proceed by

inserting $\mathbf{l}_i = \mathbf{e}_i$ into (17):

$$\begin{aligned} \langle \mathbf{M}_0 \rangle &= \begin{pmatrix} -S/\sqrt{6} + P/\sqrt{2} & 0 & 0 \\ 0 & -S/\sqrt{6} - P/\sqrt{2} & 0 \\ 0 & 0 & 2S/\sqrt{6} \end{pmatrix}, \\ \langle \mathbf{M}_1 \rangle &= \begin{pmatrix} -U/\sqrt{6} + F/\sqrt{2} & 0 & 0 \\ 0 & -U/\sqrt{6} - F/\sqrt{2} & 0 \\ 0 & 0 & 2F/\sqrt{6} \end{pmatrix}. \end{aligned} \quad (56)$$

Next, we exploit the fact that we know the structure of (58) and (59) in advance from the macroscopic considerations in Sec. IV A. We calculate all tensor invariants for constant directors by inserting (56) into (38) and (40). Since none of the terms of the macroscopic model go to zero (this was explicitly checked), we remain with all coefficients. Thus, we could collect the appropriate terms, since we already know

that both approaches need to be at least consistent, that is, if we assume constant directors in the macroscopic model, then we need to arrive at (55). We can then finally collect all terms and compare coefficients and arrive at the full biaxial energy by using our new method combining a microscopic and macroscopic approach.

This method might help to greatly simplify calculations for even more complex symmetry groups, such as for particles exhibiting molecular chirality. (At least if the primary focus is deriving microscopic expressions for coefficients and not a first-principles derivation of the structure of the free energy. The structure of the free energy, i.e., the relevant tensor invariants, is, however, essentially a solved problem for all relevant symmetry groups; see Ref. [91].) Another question to be addressed is whether the coefficients are dependent on any of the order parameters, which would render this method useless. Trivially, there cannot be an explicit dependence as only the tensor invariants depend on the order parameters. However, there might be an implicit dependence as the coefficients

might change depending on what density we use in the derivation, similarly to how certain approximations implicitly affect the resulting set of coefficients. We can, however, rule out that possibility as it is possible to use (33) instead of (32) (just with some restrictive assumptions on the tensor elements to ensure that the condition of constant directors is fulfilled) and once we evaluate the orientational integrals the coefficients still cannot depend on any tensor elements (or scalar order parameters). Since we know that both approaches have to give the same result for the restricted case, this has to be true for the general case as well.

For the dynamic equations, however, we do not use the general model but restrict ourselves to constant directors again, as this would result in a huge number of additional coefficients.

1. Ideal gas free energy

The free energy of the ideal gas (42) does not contain any gradient terms. A direct comparison to the form of (38) thus gives the general form

$$\begin{aligned} \beta \mathcal{F}_{\text{id}} = 8\pi^2 \rho_0 \int d\mathbf{R} & \left(\frac{1}{2} \left(\psi_1^2 + \frac{\text{Tr}(\langle \mathbf{M}_0 \rangle^2) + \text{Tr}(\langle \mathbf{M}_1 \rangle^2)}{5} \right) - \frac{1}{6} \left(3\psi_1 \frac{\text{Tr}(\langle \mathbf{M}_0 \rangle^2) + \text{Tr}(\langle \mathbf{M}_1 \rangle^2)}{5} + \psi_1^3 \right. \right. \\ & - \frac{2}{35} (-\sqrt{6} \text{Tr}(\langle \mathbf{M}_0 \rangle^3) + 3\sqrt{6} \text{Tr}(\langle \mathbf{M}_0 \rangle \langle \mathbf{M}_1 \rangle^2)) \Bigg) + \frac{1}{12} \left(\psi_1^4 + \frac{3}{35} \psi_1^2 (\text{Tr}(\langle \mathbf{M}_0 \rangle^2) + \text{Tr}(\langle \mathbf{M}_1 \rangle^2)) \right. \\ & - \frac{8\psi_1}{35} (-\sqrt{6} \text{Tr}(\langle \mathbf{M}_0 \rangle^3) + 3\sqrt{6} \text{Tr}(\langle \mathbf{M}_0 \rangle \langle \mathbf{M}_1 \rangle^2)) + \frac{1}{35} (3 \text{Tr}(\langle \mathbf{M}_0 \rangle^2)^2 + 3 \text{Tr}(\langle \mathbf{M}_1 \rangle^2)^2 \\ & \left. \left. - 6 \text{Tr}(\langle \mathbf{M}_0 \rangle \langle \mathbf{M}_1 \rangle^2) + 12 \text{Tr}(\langle \mathbf{M}_0 \rangle^2) \text{Tr}(\langle \mathbf{M}_1 \rangle^2)) \right) \right), \end{aligned} \quad (57)$$

which is valid even for spatially varying directors, as discussed above.

2. Excess free energy

Next, we calculate all tensor invariants presented in the bulk free energy (38) (up to second order only) and the elastic part given in (40) for constant directors to get the model for the excess free energy,

$$\begin{aligned} \mathcal{F}_{\text{exc}} = \frac{1}{2} \int d\mathbf{R} & \left(a_1 \psi_1^2 + a_2 (\nabla \psi_1)^2 + a_3 (\Delta \psi_1)^2 a(S^2 + P^2) + b(U^2 + F^2) + c(SU + PF) \right. \\ & + d \left(\sqrt{\frac{3}{2}} \left((\mathbf{l}_3 \cdot \nabla \psi_1)(\mathbf{l}_3 \cdot \nabla S) - \frac{\nabla \psi_1 \cdot \nabla S}{3} \right) + \sqrt{\frac{1}{2}} ((\mathbf{l}_1 \cdot \nabla \psi_1)(\mathbf{l}_1 \cdot \nabla P) - (\mathbf{l}_2 \cdot \nabla \psi_1)(\mathbf{l}_2 \cdot \nabla P)) \right) \\ & + e \left(\sqrt{\frac{3}{2}} \left((\mathbf{l}_3 \cdot \nabla \psi_1)(\mathbf{l}_3 \cdot \nabla U) - \frac{\nabla \psi_1 \cdot \nabla U}{3} \right) + \sqrt{\frac{1}{2}} ((\mathbf{l}_1 \cdot \nabla \psi_1)(\mathbf{l}_1 \cdot \nabla F) - (\mathbf{l}_2 \cdot \nabla \psi_1)(\mathbf{l}_2 \cdot \nabla F)) \right) \\ & + f((\nabla S)^2 + (\nabla P)^2) + g \left(\frac{(\nabla S)^2 + (\mathbf{l}_3 \cdot \nabla S)^2}{2} + \frac{(\mathbf{l}_1 \cdot \nabla P)^2 + (\mathbf{l}_2 \cdot \nabla P)^2}{2} \right) + h((\nabla U)^2 + (\nabla F)^2) \\ & + i \left(\frac{(\nabla U)^2 + (\mathbf{l}_3 \cdot \nabla U)^2}{2} + \frac{(\mathbf{l}_1 \cdot \nabla F)^2 + (\mathbf{l}_2 \cdot \nabla F)^2}{2} \right) + j((\nabla S) \cdot (\nabla U) + (\nabla P) \cdot (\nabla F)) \\ & \left. + k \left(\frac{(\nabla U) \cdot (\nabla S) + (\mathbf{l}_3 \cdot \nabla U)(\mathbf{l}_3 \cdot \nabla S)}{2} + \frac{(\mathbf{l}_1 \cdot \nabla F)(\mathbf{l}_1 \cdot \nabla P) + (\mathbf{l}_2 \cdot \nabla F)(\mathbf{l}_2 \cdot \nabla P)}{2} \right) \right) \end{aligned} \quad (58)$$

in terms of scalar order parameters and directors. Now we can compare the undetermined coefficients in (58) to the predictions from (55) and finally arrive at:

$$\begin{aligned} \mathcal{F}_{\text{exc}} = & \int d\mathbf{R} \left(a_1 \psi_1^2 + a_2 (\nabla \psi_1)^2 + a_3 (\Delta \psi_1)^2 + a \text{Tr}(\langle \mathbf{M}_0 \rangle^2) + b \text{Tr}(\langle \mathbf{M}_1 \rangle^2) + c \text{Tr}(\langle \mathbf{M}_0 \rangle \langle \mathbf{M}_1 \rangle) \right. \\ & + d(\nabla \psi_1) : (\nabla \cdot \langle \mathbf{M}_0 \rangle) + e(\nabla \psi_1) : (\nabla \cdot \langle \mathbf{M}_1 \rangle) + f(\nabla \langle \mathbf{M}_0 \rangle) : (\nabla \langle \mathbf{M}_0 \rangle) + g(\nabla \cdot \langle \mathbf{M}_0 \rangle) : (\nabla \cdot \langle \mathbf{M}_0 \rangle) \\ & \left. + h(\nabla \langle \mathbf{M}_1 \rangle) : (\nabla \langle \mathbf{M}_1 \rangle) + i(\nabla \cdot \langle \mathbf{M}_1 \rangle) : (\nabla \cdot \langle \mathbf{M}_1 \rangle) + j(\nabla \langle \mathbf{M}_0 \rangle) : (\nabla \langle \mathbf{M}_1 \rangle) + k(\nabla \cdot \langle \mathbf{M}_0 \rangle) : (\nabla \cdot \langle \mathbf{M}_1 \rangle) \right) \quad (59) \end{aligned}$$

with the coefficients

$$\begin{aligned} a_1 &= 128\pi^{\frac{9}{2}}\rho_0^2 \int d|\mathbf{R}| |\mathbf{R}|^2 \omega_{00000}(|\mathbf{R}|e_z), \\ a_2 &= -128\pi^{\frac{9}{2}}\rho_0^2 \int d|\mathbf{R}| |\mathbf{R}|^4 \omega_{00000}(|\mathbf{R}|e_z), \\ a_3 &= 128\pi^{\frac{9}{2}}\rho_0^2 \int d|\mathbf{R}| \frac{|\mathbf{R}|^6}{4!} \omega_{00000}(|\mathbf{R}|e_z), \\ a &= \frac{128\pi^{\frac{9}{2}}\rho_0^2}{25\sqrt{5}} \int d|\mathbf{R}| |\mathbf{R}|^2 \omega_{20200}(|\mathbf{R}|e_z), \\ b &= \frac{128\pi^{\frac{9}{2}}\rho_0^2}{50\sqrt{5}} \int d|\mathbf{R}| |\mathbf{R}|^2 (2\omega_{222-20}(|\mathbf{R}|e_z) + \omega_{22220}(|\mathbf{R}|e_z) + \omega_{2-22-20}(|\mathbf{R}|e_z)), \\ c &= \frac{128\pi^{\frac{9}{2}}\rho_0^2}{25\sqrt{2}\sqrt{5}} \int d|\mathbf{R}| |\mathbf{R}|^2 (\omega_{20220}(|\mathbf{R}|e_z) + \omega_{202-20}(|\mathbf{R}|e_z)), \\ d &= -\frac{64\pi^{\frac{9}{2}}\rho_0^2}{5} \sqrt{\frac{36}{45}} \int d|\mathbf{R}| \omega_{00202} |\mathbf{R}|^2 (|\mathbf{R}|e_z), \\ e &= -\frac{64\pi^{\frac{9}{2}}\rho_0^2}{5} \sqrt{\frac{36}{45}} \int d|\mathbf{R}| |\mathbf{R}|^2 (\omega_{00222}(|\mathbf{R}|e_z) + \omega_{002-22}(|\mathbf{R}|e_z)), \\ f &= -\frac{64\pi^{\frac{9}{2}}\rho_0^2}{25} \int d|\mathbf{R}| \frac{|\mathbf{R}|^4}{2} \left(\frac{4\sqrt{5}}{15} \sqrt{\frac{2}{7}} \omega_{20202}(|\mathbf{R}|e_z) + \frac{\sqrt{4}}{3} \sqrt{\frac{1}{5}} \omega_{20200}(|\mathbf{R}|e_z) \right), \\ g &= -2 \left(\frac{64\pi^{\frac{9}{2}}\rho_0^2}{25} \int d|\mathbf{R}| \frac{|\mathbf{R}|^4}{2} \left(\frac{-2\sqrt{5}}{15} \sqrt{\frac{2}{7}} \omega_{20202}(|\mathbf{R}|e_z) + \frac{\sqrt{4}}{3} \sqrt{\frac{1}{5}} \omega_{20200}(|\mathbf{R}|e_z) \right) - f \right), \\ h &= -\frac{64\pi^{\frac{9}{2}}\rho_0^2}{50} \int d|\mathbf{R}| \frac{|\mathbf{R}|^4}{2} \left(\frac{4\sqrt{5}}{15} \sqrt{\frac{2}{7}} (\omega_{22222}(|\mathbf{R}|e_z) + \omega_{2-22-22}(|\mathbf{R}|e_z) + 2\omega_{2-2222}(|\mathbf{R}|e_z)) \right. \\ & \quad \left. + \frac{\sqrt{4}}{3} \sqrt{\frac{1}{5}} (\omega_{22220}(|\mathbf{R}|e_z) + \omega_{2-22-20}(|\mathbf{R}|e_z) + 2\omega_{2-2220}(|\mathbf{R}|e_z)) \right), \\ i &= -2 \left(\frac{64\pi^{\frac{9}{2}}\rho_0^2}{50} \int d|\mathbf{R}| \frac{|\mathbf{R}|^4}{2} \left(\frac{-2\sqrt{5}}{15} \sqrt{\frac{2}{7}} (\omega_{22222}(|\mathbf{R}|e_z) + \omega_{2-22-22}(|\mathbf{R}|e_z) + 2\omega_{2-2222}(|\mathbf{R}|e_z)) \right. \right. \\ & \quad \left. \left. + \frac{\sqrt{4}}{3} \sqrt{\frac{1}{5}} (\omega_{22220}(|\mathbf{R}|e_z) + \omega_{2-22-20}(|\mathbf{R}|e_z) + 2\omega_{2-2220}(|\mathbf{R}|e_z)) \right) - h \right), \\ j &= -2 \frac{64\pi^{\frac{9}{2}}\rho_0^2}{25\sqrt{2}} \sqrt{\frac{1}{5}} \int d|\mathbf{R}| \frac{|\mathbf{R}|^4}{2} \left(\frac{4\sqrt{5}}{15} \sqrt{\frac{2}{7}} (\omega_{20222}(|\mathbf{R}|e_z) + \omega_{202-22}(|\mathbf{R}|e_z)) + \frac{\sqrt{4}}{3} \sqrt{\frac{1}{5}} (\omega_{20222} + \omega_{202-22}) \right), \\ k &= -4 \left(\frac{64\pi^{\frac{9}{2}}\rho_0^2}{25\sqrt{2}} \int d|\mathbf{R}| \frac{|\mathbf{R}|^4}{2} \left(\frac{-2\sqrt{5}}{15} \sqrt{\frac{2}{7}} (\omega_{20222}(|\mathbf{R}|e_z) + \omega_{202-22}(|\mathbf{R}|e_z)) + \frac{\sqrt{4}}{3} \sqrt{\frac{1}{5}} (\omega_{20222}(|\mathbf{R}|e_z) + \omega_{202-22}(|\mathbf{R}|e_z)) \right) - j \right) \quad (60) \end{aligned}$$

for (59). Combined with the ideal gas free energy (42), we found the most general full biaxial model in a quasimicroscopic way by explicitly calculating all tensor invariants from the macroscopic model presented in Sec. IV A for the case of constant directors and comparing terms. To arrive at the c_i and b_j introduced in Sec. IV A, we simply need to add the coefficients presented above in (60) to the coefficients in (57) if they correspond to the same term in (59). We chose this presentation as it shows more clearly

how the microscopic coefficients arise. Explicitly, the expressions for b_i are

$$\begin{aligned}
 b_1 &= \frac{4\pi^2\rho_0}{5} + \frac{a}{2}, & b_2 &= \frac{16\pi^2\rho_0}{35\sqrt{6}}, & b_3 &= \frac{2\pi^2\rho_0}{35}, \\
 b_4 &= \frac{4\pi^2\rho_0}{5} + \frac{b}{2}, & b_5 &= \frac{2\pi^2\rho_0}{35}, & b_6 &= \frac{4\pi^2\rho_0}{35}, \\
 b_7 &= 0, & b_8 &= \frac{c}{2}, & b_9 &= 0, & b_{10} &= 0, & b_{11} &= 0, \\
 b_{12} &= 0, & b_{13} &= \frac{8\pi^2\rho_0}{35}, & b_{14} &= 4\pi^2\rho_0 + \frac{a_1}{2}, \\
 b_{15} &= \frac{-4\pi^2\rho_0}{3}, & b_{16} &= \frac{8\pi^2\rho_0}{35}, & b_{17} &= 0, \\
 b_{18} &= \frac{-4\pi^2\rho_0}{5}, & b_{19} &= \frac{-4\pi^2\rho_0}{5}, & b_{20} &= \frac{16\sqrt{6}\pi^2\rho_0}{105}, \\
 b_{21} &= 0, & b_{22} &= \frac{-16\sqrt{6}\pi^2\rho_0}{35}, & b_{23} &= 0, & b_{24} &= \frac{2\pi^2\rho_0}{35}, \\
 b_{25} &= \frac{2\pi^2\rho_0}{35}, & b_{26} &= 0,
 \end{aligned} \tag{61}$$

and the expressions for c_i are

$$\begin{aligned}
 c_1 &= \frac{a_2}{2}, & c_2 &= \frac{f}{2}, & c_3 &= \frac{j}{2}, & c_4 &= \frac{h}{2}, & c_5 &= \frac{g}{2}, \\
 c_6 &= \frac{k}{2}, & c_7 &= \frac{i}{2}, & c_8 &= \frac{e}{2}, & c_9 &= \frac{d}{2}, & c_{10} &= \frac{a_3}{2}.
 \end{aligned} \tag{62}$$

F. Model 2

The second microscopic model we will consider for the explicit derivation of dynamic equations is a full theory for ψ_1 , $\langle \mathbf{M}_0 \rangle_{ij}$, and their coupling. This means that we go beyond earlier PFC models only describing uniaxial phases (such as Refs. [54,59]) and introduce phase biaxiality by using the order parameter P . We, however, neglect the second tensor order parameter $\langle \mathbf{M}_1 \rangle$ and work only with $\langle \mathbf{M}_0 \rangle$. Thus, we can arrive at this model by taking the results from Sec. IV E and setting $\langle \mathbf{M}_1 \rangle$ to $\mathbf{0}$. This special case describes the important situation of uniaxial particles in the most general way, not fully presented in the PFC model literature so far. (As an alternate derivation for this model, one could also argue that the coefficients from Refs. [54,59] are, if formulated through the nematic tensor, still valid, as its symmetry does not change with the inclusion of the additional order parameter P . This is a bit similar to the discussion given below (60). In that case, however, we would need to adapt our definition of the order parameters as they vary slightly in the chosen convention.)

We begin by writing

$$\rho = \rho_0(1 + \psi_1 + \langle \mathbf{M}_0 \rangle : \mathbf{M}_0) \tag{63}$$

and consider the full three-dimensional nematic tensor for uniaxial particles,

$$\langle \mathbf{M}_0 \rangle = \sqrt{\frac{3}{2}}S \left(\mathbf{l}_3 \otimes \mathbf{l}_3 - \frac{1}{3}\mathbf{I} \right) + \frac{P}{\sqrt{2}}(\mathbf{l}_1 \otimes \mathbf{l}_1 - \mathbf{l}_2 \otimes \mathbf{l}_2), \tag{64}$$

where by including the order parameter P and the director $\mathbf{l}_2$ we also allow for the description of biaxial phases (see

Sec. II A for a discussion of the difference between biaxial phases and biaxial particles).

1. Ideal gas free energy

The ideal gas free energy is given by

$$\begin{aligned}
 \beta \mathcal{F}_{\text{id}} &= 8\pi^2\rho_0 \int d\mathbf{R} \left(\frac{1}{2} \left(\psi_1^2 + \frac{S^2 + P^2}{5} \right) \right. \\
 &\quad - \frac{1}{6} \left(\psi_1^3 + \frac{3\psi_1}{5}(S^2 + P^2) - \frac{2}{35}(3P^2S - S^3) \right) \\
 &\quad + \frac{1}{12} \left(\psi_1^4 + \frac{3(S^4 + P^4)}{35} + \psi_1^2 \frac{6(S^2 + P^2)}{5} \right. \\
 &\quad \left. \left. - \frac{2}{35}\psi_1(12P^2S - 4S^3) + \frac{6S^2P^2}{35} \right) \right),
 \end{aligned}$$

which equals (57) when dropping the terms involving $\langle \mathbf{M}_1 \rangle$. This can be seen by inserting (64). (The tensor invariants not involving any derivatives do not have any director dependence.) Alternatively, one can also use (42) and set $U = F = 0$. This can be cross-checked by performing a Taylor expansion of the logarithm and integrating out orientational degrees of freedom of (41), as discussed in Sec. IV B.

2. Excess free energy

The excess free energy is then

$$\begin{aligned}
 \mathcal{F}_{\text{exc}} &= \int d\mathbf{R} (a_1\psi_1^2 + a_2(\nabla\psi_1)^2 + a_3(\Delta\psi_1)^2 \\
 &\quad + a \text{Tr}(\langle \mathbf{M}_0 \rangle^2) + d(\nabla\psi_1) : (\nabla \cdot \langle \mathbf{M}_0 \rangle) \\
 &\quad + f(\nabla \cdot \langle \mathbf{M}_0 \rangle) : (\nabla \cdot \langle \mathbf{M}_0 \rangle) \\
 &\quad + g(\nabla \langle \mathbf{M}_0 \rangle) : (\nabla \langle \mathbf{M}_0 \rangle)),
 \end{aligned} \tag{65}$$

where the parameters are given in (60). This could also be written explicitly in terms of S , P , and the three directors, as in (58).

This free energy does not only include the Frank elastic energy

$$\begin{aligned}
 \mathcal{F}_{\text{Frank}, \mathbf{l}_3} &= \frac{1}{2} \int d\mathbf{R} (K_{1,S}(\nabla \cdot \mathbf{l}_3)^2 + K_{2,S}(\mathbf{l}_3 \cdot (\nabla \times \mathbf{l}_3))^2 \\
 &\quad + K_{3,S}(\mathbf{l}_3 \times (\nabla \times \mathbf{l}_3))^2),
 \end{aligned} \tag{66}$$

coming from contributions of the uniaxial director $\mathbf{l}_3$, but also gives expressions for the elastic energy for the directors $\mathbf{l}_2$ and $\mathbf{l}_1$. Taking, for instance, the director $\mathbf{l}_2$, the elastic energy would include, for example, the term

$$\begin{aligned}
 \mathcal{F}_{\text{Frank}, \mathbf{l}_2} &= \frac{1}{2} \int d\mathbf{R} (K_{1,P}(\nabla \cdot \mathbf{l}_2)^2 + K_{2,P}(\mathbf{l}_2 \cdot (\nabla \times \mathbf{l}_2))^2 \\
 &\quad + K_{3,P}(\mathbf{l}_2 \times (\nabla \times \mathbf{l}_2))^2).
 \end{aligned} \tag{67}$$

The Frank coefficients are then given by

$$\begin{aligned}
 K_{1,S} &= \sqrt{\frac{3}{2}} S^2 \cdot \tilde{K}_{1,S}, \\
 K_{2,S} &= \sqrt{\frac{3}{2}} S^2 \cdot \tilde{K}_{2,S}, \\
 K_{3,S} &= K_{1,S}, \\
 K_{1,P} &= \sqrt{\frac{1}{2}} P^2 \cdot \tilde{K}_{1,P}, \\
 K_{2,P} &= \sqrt{\frac{1}{2}} P^2 \cdot \tilde{K}_{2,P}, \\
 K_{3,P} &= K_{1,P},
 \end{aligned} \tag{68}$$

where the unique relation between K_i and the elastic coefficients f and g (also commonly denoted as L_1 and L_2 in the literature) in (59) is given by

$$\begin{aligned}
 \tilde{K}_{1,S} &= 2f + g, \\
 \tilde{K}_{2,S} &= 2f, \\
 \tilde{K}_{1,P} &= 2h + i, \\
 \tilde{K}_{2,P} &= 2h.
 \end{aligned} \tag{69}$$

The degeneracy of $K_{1,Y} = K_{3,Y}$ is an artifact of our expansion, which should be resolved in higher orders, as in the uniaxial case [94]. We see that there generally appear different kinds of Frank constants in biaxial systems. In the most general theory, involving both tensor order parameters, there will be complex coupling between all four S, U, P, F parameters and their directors as seen in Sec. IV A.

V. DYNAMICAL FIELD THEORIES

A. General ingredients

Having expressed the free energy in terms of the orientational order parameters, we now derive the corresponding dynamic equations for Model 1 and Model 2. In both cases, our starting point is the DDFT for biaxial particles given by Eq. (6). If we want to derive dynamical equations for the orientational order parameters, then we will have to take an orientational average of Eq. (6). For doing this, we need to know the form of the diffusion tensor $\mathbf{D}(\mathbf{O})$ appearing in this equation.

Since calculating the diffusion tensor is in general not analytically possible, we use as an approximation the form known for hard rods. This is reasonable as long as the particles' diffusion behavior is sufficiently similar to that of rods or spheres (the diffusion tensor for rods contains that of spheres as a limiting case), which should be the case if, for instance, the particles are long and thin cuboids (similar to rods) or if they are cubes (similar to spheres). If the particle shape is different, then the qualitative form of the obtained field theory will still be correct as long as translation-diffusion-coupling can be neglected, but the values of the mobility coefficients may be less accurate. An explicit assumption about the form of $\mathbf{D}$ is required primarily to be able to analytically derive the dynamical equations for our order parameters in closed form.

The diffusion tensor of hard rods is given by [97]

$$\begin{aligned}
 \mathbf{D}_{\text{TR}} &= \mathbf{D}_{\text{RT}} = \mathbf{0}, \\
 \mathbf{D}_{\text{TT}} &= D_{\parallel} \mathbf{m}_3 \otimes \mathbf{m}_3 + D_{\perp} (\mathbf{I} - \mathbf{m}_3 \otimes \mathbf{m}_3), \\
 \mathbf{D}_{\text{RR}} &= D_{\text{R}} \mathbf{I}.
 \end{aligned} \tag{70}$$

Here $\mathbf{0}$ is a tensor where all entries are zero, and $\mathbf{m}_3$ and could be represented by

$$\mathbf{m}_3 = R \cdot (0, 0, 1)^T, \tag{71}$$

which, using Eq. (14), is given by

$$\mathbf{m}_3 = (\cos(\phi) \sin(\theta), \sin(\phi) \sin(\theta), \cos(\theta)). \tag{72}$$

The explicit formulas for $D_{\parallel}$ (parallel translational diffusion coefficient), $D_{\perp}$ (perpendicular translational diffusion coefficient), and D_{R} (rotational diffusion coefficient) are (see Ref. [97])

$$D_{\parallel} = \frac{k_B T}{\gamma_{\parallel}}, \quad D_{\perp} = \frac{k_B T}{\gamma_{\perp}}, \quad D_{\text{R}} = \frac{k_B T}{\gamma_{\text{R}}}. \tag{73}$$

Further,

$$\gamma_{\text{R}} = \frac{\pi \eta L^3}{3} \ln\left(\frac{L}{D}\right), \quad \gamma_{\parallel} = \frac{2\pi \eta L}{\ln\left(\frac{L}{D}\right)}, \quad \gamma_{\perp} = 2\gamma_{\parallel}. \tag{74}$$

In this case, L and D are the length and diameter of the rod, respectively, and η denotes the viscosity of the surrounding solvent.

B. Model 1: PFC for scalar order parameters

1. Full formulation

Having clarified the necessary prerequisites for the usage of DDFT, we can derive dynamical equations for Model 1 in terms of our scalar order parameters. We start by taking the first time derivative of the definition (9) of a generic scalar order parameter Y and insert (6):

$$\partial_t Y = \frac{2l_Y + 1}{8\pi^2 \rho_0} \int d\mathbf{O} f_Y(\mathbf{O}) \beta \nabla_{\mathbf{R}} \cdot \left(D(\mathbf{O}) \rho \nabla_{\mathbf{R}} \frac{\delta \mathcal{F}}{\delta \rho} \right). \tag{75}$$

Here the free energy has the form given in (55) added to (65). We assume $l_Y = 2$ for $Y \in S, U, P, F$ and $l_Y = 0$ for $Y = \psi_1$. Next, we use the relation

$$\frac{\delta \mathcal{F}}{\delta \rho} = \sum_Y \frac{2l_Y + 1}{\rho_0 8\pi^2} f_Y \frac{\delta \mathcal{F}}{\delta Y} \tag{76}$$

and insert

$$\rho = \rho_0 \left(1 + \sum_Y f_Y Y \right) \tag{77}$$

with $Y \in \psi_1, S, U, P, F$ into Eq. (75). Moreover, we define the coefficients

$$\begin{aligned}
 \tilde{M}_{XYZ}^{(\text{D}_{\text{TT}})} &= \frac{(2l_Y + 1)(2l_Z + 1)}{64\pi^4 \rho_0} \int_{\text{SO}(3)} d\mathbf{O} \\
 &\quad \times D_{\text{TT}}(\mathbf{O}) f_Y(\mathbf{O}) f_X(\mathbf{O}) f_Z(\mathbf{O}), \\
 \tilde{M}_{XYZ}^{(\text{D}_{\text{RR}})} &= \frac{(2l_Y + 1)(2l_Z + 1)}{64\pi^4 \rho_0} \int_{\text{SO}(3)} d\mathbf{O} D_{\text{RR}} f_Y(\mathbf{O}) \\
 &\quad \times \nabla_{\mathbf{O}} \cdot (f_X(\mathbf{O}) \nabla_{\mathbf{O}} f_Z(\mathbf{O}))
 \end{aligned} \tag{78}$$

with $X, Y, Z \in \{\psi_1, S, U, P, F\}$ and (once again) the convention $f_{\psi_1} = 1$. The parameter l_X is 0 for $X = \psi_1$ and 2 else. After evaluating the orientational integrals in Eq. (75), we arrive at the final result

$$\partial_t Y = \beta \nabla \cdot \left(\sum_{X,Z} X \tilde{M}_{YXZ}^{(D_{TT})} \nabla \frac{\delta \mathcal{F}}{\delta Z} \right) + \beta \sum_{X,Z} \tilde{M}_{YXZ}^{(D_{RR})} X \frac{\delta \mathcal{F}}{\delta Z}. \quad (79)$$

The coefficients can be easily calculated with the integrals presented in Appendix A.

2. Constant mobility approximation

One important approximation used in many PFC models is the so-called constant mobility approximation, where we assume the density-dependent mobility of (6) to be constant, that is, we set $\beta D \rho \approx \beta D \rho_0$ to arrive at

$$\partial_t \rho = \rho_0 \beta \nabla \mathcal{R} \cdot D(\mathbf{O}) \cdot \nabla \mathcal{R} \frac{\delta \mathcal{F}}{\delta \rho}. \quad (80)$$

We will now use (80) by inserting it into the first time derivative of (10) to proceed with the derivation of our new simplified models.

Using the constant mobility approximation, we arrive at

$$\partial_t Y = \beta \nabla \cdot \sum_Z M_{Y\psi_1 Z}^{(D_{TT})} \nabla \frac{\delta \mathcal{F}}{\delta Z} + \beta \sum_Z M_{Y\psi_1 Z}^{(D_{RR})} \frac{\delta \mathcal{F}}{\delta Z}. \quad (81)$$

This model is drastically simpler than the previously presented full DDFT model given by Eq. (79), since the summation over X vanishes completely. This leads to a much smaller number of terms in (79) and thus less coefficients to be calculated.

C. Model 2: PFC for tensorial order parameters

Here we derive equations for the dynamics of the uniaxial nematic tensor $\langle M_0 \rangle_{ij}$ in Model 2. As the number of required coefficients is quite large, we only consider the constant mobility approximation explained in Sec. VB. Doing so, we arrive at the following dynamic equations, extending results obtained for the special case $P = 0$ in Ref. [98]:

$$\begin{aligned} \partial_t \psi_1 &= \frac{1}{8\pi^2 \rho_0} \int d\mathbf{O} \left(\beta \nabla^2 \left(\rho_0 D_{TT}(\mathbf{O}) \frac{\delta \mathcal{F}}{\delta \rho} \right) \right. \\ &\quad \left. + D_{RR} \nabla_{\mathbf{O}}^2 \rho_0 \frac{\delta \mathcal{F}}{\delta \rho} \right), \\ \partial_t \langle M_0 \rangle_{ij} &= \frac{5}{8\pi^2 \rho_0} \int d\mathbf{O} \sqrt{\frac{3}{2}} \left(m_{3,i} m_{3,j} - \frac{1}{3} \right) \\ &\quad \times \left(\beta \nabla^2 \rho_0 \left(D_{TT}(\mathbf{O}) \frac{\delta \mathcal{F}}{\delta \rho} \right) + D_{RR} \nabla_{\mathbf{O}}^2 \rho_0 \frac{\delta \mathcal{F}}{\delta \rho} \right). \end{aligned} \quad (82)$$

By using the relation

$$\frac{\delta \mathcal{F}}{\delta \rho} = \frac{1}{8\pi^2 \rho_0} \frac{\delta \mathcal{F}}{\delta \psi_1} + \frac{5}{8\pi^2 \rho_0} \sqrt{\frac{3}{2}} \left(m_{3,i} m_{3,j} - \frac{1}{3} \right) \frac{\delta \mathcal{F}}{\delta \langle M_0 \rangle_{ij}}, \quad (83)$$

we can use the microscopic definition of the order parameters in Eq. (9) to arrive at

$$\begin{aligned} \partial_t \psi_1 &= \beta \nabla \cdot \sum_Z \tilde{M}_{\psi_1, Z}^{(D_{TT})} \nabla \frac{\delta \mathcal{F}}{\delta Z}, \\ \partial_t \langle M_0 \rangle_{ij} &= \beta \nabla \cdot \sum_Z \tilde{M}_{\langle M_0 \rangle_{ij}, Z}^{(D_{TT})} \nabla \frac{\delta \mathcal{F}}{\delta Z} + \beta \sum_Z \tilde{M}_{\langle M_0 \rangle_{ij}, Z}^{(D_{RR})} \frac{\delta \mathcal{F}}{\delta Z}, \\ Z &\in \{\psi_1, \langle M_0 \rangle_{ij}\}, \end{aligned} \quad (84)$$

where the coefficients are defined as

$$\begin{aligned} \tilde{M}_{X,Z}^{(D_{TT})} &= \frac{(2l_X + 1)(2l_Z + 1)}{64\pi^4 \rho_0} \\ &\quad \times \int_{\text{SO}(3)} d\mathbf{O} f_X(\mathbf{O}) f_Z(\mathbf{O}) D_{TT}(\mathbf{O}), \\ \tilde{M}_{X,Z}^{(D_{RR})} &= \frac{(2l_X + 1)(2l_Z + 1)}{64\pi^4 \rho_0} \\ &\quad \times \int_{\text{SO}(3)} d\mathbf{O} f_X(\mathbf{O}) \nabla_{\mathbf{O}}^2 f_Z(\mathbf{O}), \\ f_{\langle M_0 \rangle_{ij}} &= \sqrt{\frac{3}{2}} \left(m_{3,i} m_{3,j} - \frac{1}{3} \right), \\ f_{\psi_1} &= 1. \end{aligned} \quad (85)$$

The integrals necessary for the coefficients are given in detail in Appendix B. [One might wonder why we chose to integrate over $\text{SO}(3)$, instead of S_2 , as only two angles are relevant. This is done simply to ensure a unified notation—since the distributions do not depend on χ here, the additional integral over χ simply contributes an extra factor 2π , which is canceled by our normalization, as explained in the comment below (36).]

Note that the form of (84) implies that only ψ_1 is conserved (due to mass conservation) but not $\langle M_0 \rangle_{ij}$. This is because the coefficients $\tilde{M}_{X,Z}^{(D_{RR})}$ vanish only for $X = \psi_1$. In this case, coefficients of this type do not appear, as they are proportional to the angular derivative of a constant function, which is obviously 0. This is, however, not the case for all other order parameters, whose microscopic definition is weighted with some angular function. For the scalar order parameters S, U, P, F , this would be the corresponding Mulder matrix; for a tensor order parameter element $\langle M_0 \rangle_{ij}$, this would be $\sqrt{\frac{3}{2}} (m_{3,i} m_{3,j} - \frac{1}{3})$.

VI. APPLICATION: RELAXATION TO EQUILIBRIUM

To demonstrate the practical usefulness of our model, we study as a simple application the relaxation of the system to isotropic equilibrium. Since in previous work [31] the homogeneous equilibrium states of biaxial liquid crystals were classified via the order parameters S, U, P , and F , a natural scenario to consider is a spatially homogeneous version of Model 1 (which is basically a nonequilibrium extension of the work in Ref. [31]).

To do this we make the following assumptions: First, our initial state is characterized by order parameters not dependent on position, i.e., $X \neq X(\mathbf{R})$. This in particular implies $\psi_1 = 0$ for all times and all gradient terms vanish. Second, we set

the parameters $P = U = 0$ for the moment, as these are less relevant in many systems of interest (for details see Ref. [31]). Third, we assume that the perturbation from the isotropic equilibrium state is small. This means we limit ourselves to second-order terms and ignore all higher contributions. (As a short note, one further reason our restriction to second order is sensible is that this is the only way a dynamic equation using the constant mobility approximation can reproduce the diffusion equation in the noninteracting limit—for details and a further explanation see Ref. [52].) We thus arrive at a free energy of the form

$$\mathcal{F} = \int d\mathbf{R} \int d\mathbf{O} (b_1 S^2 + b_4 F^2) \quad (86)$$

using the coefficients b_1 and b_4 from Eq. (61). Inserting Eq. (86) into Eq. (81) then gives

$$\begin{aligned} \partial_t S &= \beta b_1 M_{S\psi_1 S}^{(D_{RR})} S, \\ \partial_t F &= \beta b_4 M_{F\psi_1 F}^{(D_{RR})} F, \end{aligned} \quad (87)$$

which has the solution

$$\begin{aligned} S(t) &= S_0 e^{\lambda_1 t}, \\ F(t) &= F_0 e^{\lambda_2 t} \end{aligned} \quad (88)$$

with initial perturbation amplitudes S_0 and F_0 and relaxation rates

$$\begin{aligned} \lambda_1 &= \frac{5}{64\pi^4 \rho_0} \beta b_1 D_R \left(-\frac{3}{2} \pi^2 \right), \\ \lambda_2 &= \frac{5}{64\pi^4 \rho_0} \beta b_4 D_R \left(-\frac{126}{35} \pi^2 \right). \end{aligned} \quad (89)$$

Thus, in this simple model, the parameters simply show independent exponential relaxation to equilibrium. While this result is not very surprising, the value of our model lies in the availability of explicit analytical predictions for the relaxation rates. In leading order, we have $\lambda_1, \lambda_2 \propto \rho_0$ (since $b_1 \propto \rho_0^2$ and $b_4 \propto \rho_0^2$) and further $\lambda_1, \lambda_2 \propto D_R$. This means that higher densities and higher diffusion rates decrease the characteristic timescale on which the system relaxes to equilibrium, as is expected from physical intuition. Note that S and F relax on different timescales.

We now consider the more complicated case that also P and U are nonzero, once again with the coefficients given in (61):

$$\begin{aligned} \mathcal{F} &= \int d\mathbf{R} \int d\mathbf{O} (b_1 (S^2 + P^2) + b_4 (F^2 + U^2) \\ &\quad + b_9 (SU + PF)). \end{aligned} \quad (90)$$

Inserting Eq. (90) into Eq. (81) results in

$$\begin{aligned} \partial_t S &= \beta (b_1 M_{S\psi_1 S}^{(D_{RR})} + b_9 M_{S\psi_1 U}^{(D_{RR})}) S + \beta b_9 M_{S\psi_1 P}^{(D_{RR})} U, \\ \partial_t U &= \beta b_9 M_{U\psi_1 S}^{(D_{RR})} S + \beta (b_4 M_{U\psi_1 U}^{(D_{RR})} + b_9 M_{U\psi_1 P}^{(D_{RR})}) U \end{aligned} \quad (91)$$

and

$$\begin{aligned} \partial_t P &= \beta (b_1 M_{P\psi_1 P}^{(D_{RR})} + b_9 M_{P\psi_1 F}^{(D_{RR})}) P + \beta b_9 M_{P\psi_1 U}^{(D_{RR})} F, \\ \partial_t F &= \beta b_9 M_{F\psi_1 P}^{(D_{RR})} P + \beta (b_4 M_{F\psi_1 F}^{(D_{RR})} + b_9 M_{F\psi_1 U}^{(D_{RR})}) F. \end{aligned} \quad (92)$$

Somewhat surprisingly, the equations decouple into two independent sets of ODEs. Mathematically, this is because we expanded both $\langle \mathbf{M}_0 \rangle$ and $\langle \mathbf{M}_1 \rangle$ into the orthonormal base $\{\mathbf{L}_0, \mathbf{L}_1\}$, so the only bulk coupling term allowed by symmetry, which is $\langle \mathbf{M}_0 \rangle \cdot \langle \mathbf{M}_1 \rangle$, resolves to be $SU + PF$ for constant directors.

It is clear that the respective coupling of S and U as well as F and P in the free energy (90) leads to a coupling in the analytic solutions $X(t) \in \{S, U, P, F\}$ as well. The intuitive reason might be that both S and U measure uniaxial phases and cannot detect the onset of biaxial order, whereas as both F and P are only nonzero in biaxial phases. More explicitly, we can write Eq. (92) as matrix equation in the form

$$\begin{aligned} \partial_t \begin{pmatrix} S \\ U \end{pmatrix} &= \begin{pmatrix} k_1 & k_2 \\ k_3 & k_4 \end{pmatrix} \begin{pmatrix} S \\ U \end{pmatrix}, \\ \partial_t \begin{pmatrix} P \\ F \end{pmatrix} &= \begin{pmatrix} l_1 & l_2 \\ l_3 & l_4 \end{pmatrix} \begin{pmatrix} P \\ F \end{pmatrix}, \end{aligned} \quad (93)$$

with coefficients k_i and l_i that can be read off from Eq. (92). Equation (93) has the following analytical solution for the order parameters S and U :

$$\begin{aligned} S(t) &= c_1^{(S,U)} k_2 e^{\lambda_1^{(S,U)} t} + c_2^{(S,U)} k_2 e^{\lambda_2^{(S,U)} t}, \\ U(t) &= c_1^{(S,U)} (\lambda_1^{(S,U)} - k_1) e^{\lambda_1^{(S,U)} t} + c_2^{(S,U)} (\lambda_2^{(S,U)} - k_1) e^{\lambda_2^{(S,U)} t} \end{aligned} \quad (94)$$

with eigenvalues

$$\begin{aligned} \lambda_1^{(S,U)} &= \frac{k_1 + k_4 + \sqrt{(k_1 - k_4)^2 + 4k_2 k_3}}{2}, \\ \lambda_2^{(S,U)} &= \frac{k_1 + k_4 - \sqrt{(k_1 - k_4)^2 + 4k_2 k_3}}{2}. \end{aligned} \quad (95)$$

Here $c_1^{(S,U)}$ and $c_2^{(S,U)}$ are coefficients that are determined through initial conditions. Similarly, for the order parameters P and F we have

$$\begin{aligned} P(t) &= c_1^{(P,F)} l_2 e^{\lambda_1^{(P,F)} t} + c_2^{(P,F)} l_2 e^{\lambda_2^{(P,F)} t}, \\ F(t) &= c_1^{(P,F)} (\lambda_1^{(P,F)} - l_1) e^{\lambda_1^{(P,F)} t} + c_2^{(P,F)} (\lambda_2^{(P,F)} - l_1) e^{\lambda_2^{(P,F)} t} \end{aligned} \quad (96)$$

with eigenvalues

$$\begin{aligned} \lambda_1^{(P,F)} &= \frac{l_1 + l_4 + \sqrt{(l_1 - l_4)^2 + 4l_2 l_3}}{2}, \\ \lambda_2^{(P,F)} &= \frac{l_1 + l_4 - \sqrt{(l_1 - l_4)^2 + 4l_2 l_3}}{2}. \end{aligned} \quad (97)$$

In conclusion, we have demonstrated how our theory can analytically predict an exponential relaxation to equilibrium starting from a small homogeneous perturbation. For a simultaneous relaxation of all four orientational order parameters S, U, P , and F , we find that only S and U as well as P and F are coupled, respectively.

VII. CONCLUSION

Starting from the general form of a DDFT for biaxial particles [46], we have derived PFC models for the coupled

dynamics of the orientational order parameters S , U , P , and F relevant for biaxial particles [31,73] (Model 1) and for the dynamics of the full nematic tensor of uniaxial particles that can form biaxial phases (Model 2). We moreover demonstrated that the derivation gives the correct coefficients in the free energy also for general biaxial liquid crystals. The models derived here provide a general description of spatially inhomogeneous orientational ordering dynamics in nonpolar systems and allow to simulate it more efficiently than previously existing theories, such as DDFT. It is also more general than previous PFC models for uniaxial liquid crystals [54]. Despite this, it still remains a theory based on first principles, unlike macroscopic theories that have to get numerical values for the coefficients elsewhere, such as in experiments or simulations [91].

We have also demonstrated that our models can be used to analytically characterize the relaxation dynamics to equilibrium. The next step would be a numerical implementation and investigation of the models derived here. Moreover, one could extend the theory towards the active case to obtain a biaxial active PFC model. Finally, one could investigate particles with lower symmetry class. The method proposed in this work allows to do this with a significantly reduced derivation effort, allowing to perform previously unattempted derivations.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [99].

APPENDIX A: COEFFICIENTS FOR MODEL 1

In this section, we list and compute all of the integrals needed for the coefficients $\tilde{M}_{XYZ}^{(D_{TT})}$ and $\tilde{M}_{XYZ}^{(D_{RR})}$ defined in (78) and the spherical harmonics integrals mentioned earlier.

1. Taylor expansion

In Sec. IV D 2 we derived the excess free energy for a system of biaxial liquid crystals with constant directors. In order to approximately calculate a convolution integral appearing in this derivation, we need to perform a gradient expansion, which involves calculating several angular integrals. We now give all integrals necessary for the gradient expansion. For the second order of the gradient expansion we need the following

integrals:

$$\begin{aligned} \int_{S_2} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 Y_{22}(\mathbf{O}) &= \begin{pmatrix} \sqrt{2\pi/15} & i\sqrt{2\pi/15} & 0 \\ i\sqrt{2\pi/15} & -\sqrt{2\pi/15} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\ \int_{S_2} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 Y_{20}(\mathbf{O}) &= \text{diag}\left(-2\frac{\sqrt{5\pi}}{15}, -2\frac{\sqrt{5\pi}}{15}, 4\frac{\sqrt{5\pi}}{15}\right), \\ \int_{S_2} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 Y_{2-2}(\mathbf{O}) &= \begin{pmatrix} \sqrt{2\pi/15} & -i\sqrt{2\pi/15} & 0 \\ -i\sqrt{2\pi/15} & -\sqrt{2\pi/15} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\ \int_{S_2} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 Y_{00}(\mathbf{O}) &= \text{diag}\left(\frac{\sqrt{4\pi}}{3}, \frac{\sqrt{4\pi}}{3}, \frac{\sqrt{4\pi}}{3}\right). \end{aligned} \quad (\text{A1})$$

For zeroth order of the gradient expansion we need the following integral:

$$\int_{S_2} d\mathbf{O} Y_{lm}(\mathbf{O}) = \delta_{l0}\delta_{m0}\sqrt{4\pi}. \quad (\text{A2})$$

Here i denotes the imaginary unit.

2. Translational diffusion

When deriving dynamic equations for the order parameters, the coefficients of the resulting terms can be calculated analytically, which involves a number of angular integrals. This involves two distinct parts: translational and rotational diffusion, which are calculated in two different manners, as explained in (78). Now, we give all integrals necessary for the translational diffusion coefficients:

$$\begin{aligned} \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 f_S(\mathbf{O}) f_S(\mathbf{O}) f_S(\mathbf{O}) &= \frac{8\pi^2}{105} \text{diag}(-1, -1, 8), \\ \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 f_S(\mathbf{O}) f_U(\mathbf{O}) f_U(\mathbf{O}) &= \text{diag}\left(\frac{-8\pi^2}{35}, \frac{-8\pi^2}{35}, 0\right), \\ \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_U(\mathbf{O}) f_P(\mathbf{O}) &= 0, \\ \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_U(\mathbf{O}) f_F(\mathbf{O}) &= \frac{4\sqrt{3}\pi^2}{105} \text{diag}(-1, 1, 0), \\ \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_S(\mathbf{O}) f_U(\mathbf{O}) &= 0, \end{aligned}$$

$$\begin{aligned}
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 f_S(\mathbf{O}) f_S(\mathbf{O}) f_P(\mathbf{O}) \\
 &= \frac{8\sqrt{3}\pi^2}{105} \text{diag}(1, -1, 0), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_P(\mathbf{O}) f_P(\mathbf{O}) \\
 &= \text{diag}\left(\frac{-8\pi^2}{35}, \frac{-8\pi^2}{35}, 0\right), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_P(\mathbf{O}) f_F(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_S(\mathbf{O}) f_F(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_F(\mathbf{O}) f_F(\mathbf{O}) \\
 &= \text{diag}\left(0, 0, \frac{16\pi^2}{35}\right), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_U(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_F(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_S(\mathbf{O}) \\
 &= \text{diag}\left(\frac{8\pi^2}{21}, \frac{8\pi^2}{21}, \frac{88\pi^2}{105}\right), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_P(\mathbf{O}) \\
 &= \frac{16\sqrt{3}\pi^2}{105} \text{diag}(-1, 1, 0), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_S(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_{\psi_1}(\mathbf{O}) \\
 &= \frac{8\pi^2}{15} \text{diag}(-1, -1, 2), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_P(\mathbf{O}) f_P(\mathbf{O}) f_P(\mathbf{O}) \\
 &= \frac{8\sqrt{3}\pi^2}{35} \text{diag}(1, -1, 0), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_P(\mathbf{O}) f_P(\mathbf{O}) f_{\psi_1}(\mathbf{O}) \\
 &= \text{diag}\left(\frac{24\pi^2}{35}, \frac{24\pi^2}{35}, \frac{8\pi^2}{35}\right), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_P(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_{\psi_1}(\mathbf{O}) \\
 &= \text{diag}\left(\frac{8\sqrt{3}\pi^2}{15}, -\frac{8\sqrt{3}\pi^2}{15}, 0\right), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_P(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_F(\mathbf{O}) = \mathbf{0},
 \end{aligned}$$

$$\begin{aligned}
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_P(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_U(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 f_P(\mathbf{O}) f_F(\mathbf{O}) f_U(\mathbf{O}) \\
 &= \text{diag}\left(\frac{4\pi^2}{21}, \frac{4\pi^2}{21}, \frac{8\pi^2}{105}\right), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_P(\mathbf{O}) f_P(\mathbf{O}) f_U(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_P(\mathbf{O}) f_P(\mathbf{O}) f_F(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_U(\mathbf{O}) f_U(\mathbf{O}) f_U(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_U(\mathbf{O}) f_U(\mathbf{O}) f_{\psi_1}(\mathbf{O}) \\
 &= \text{diag}\left(\frac{24\pi^2}{35}, \frac{24\pi^2}{35}, \frac{8\pi^2}{35}\right), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_U(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_{\psi_1}(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_U(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_F(\mathbf{O}) \\
 &= \frac{16\sqrt{3}\pi^2}{105} \text{diag}(1, -1, 0), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_U(\mathbf{O}) f_U(\mathbf{O}) f_F(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_U(\mathbf{O}) f_F(\mathbf{O}) f_F(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_F(\mathbf{O}) f_F(\mathbf{O}) f_F(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_F(\mathbf{O}) f_F(\mathbf{O}) f_{\psi_1}(\mathbf{O}) \\
 &= \text{diag}\left(\frac{8\pi^2}{21}, \frac{8\pi^2}{21}, \frac{88\pi^2}{105}\right), \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_F(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_{\psi_1}(\mathbf{O}) = \mathbf{0}, \\
 & \int_{\text{SO}(3)} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_{\psi_1}(\mathbf{O}) f_{\psi_1}(\mathbf{O}) f_{\psi_1}(\mathbf{O}) \\
 &= \text{diag}\left(\frac{4\pi^2}{3}, \frac{4\pi^2}{3}, \frac{4\pi^2}{3}\right).
 \end{aligned}$$

All other integrals for translational diffusion follow from symmetry, e.g., $\int d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_X(\mathbf{O}) f_Y(\mathbf{O}) f_Z(\mathbf{O})$ is equal to $\int d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 \cdot f_Y(\mathbf{O}) f_X(\mathbf{O}) f_Z(\mathbf{O})$.

3. Rotational diffusion

The aforementioned symmetry does not apply to rotational diffusion due to the different structure of the integrals involving angular derivatives. We now give all integrals necessary

[illegible]

[illegible]

$$\begin{aligned}
\int_{\text{SO}(3)} d\mathbf{O} f_F(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_P(\mathbf{O}) \nabla_{\mathbf{O}} f_S(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_F(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_P(\mathbf{O}) \nabla_{\mathbf{O}} f_U(\mathbf{O})) &= -\frac{4}{7}\pi^2, \\
\int_{\text{SO}(3)} d\mathbf{O} f_F(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_P(\mathbf{O}) \nabla_{\mathbf{O}} f_P(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_F(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_P(\mathbf{O}) \nabla_{\mathbf{O}} f_F(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_F(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_{\psi_1}(\mathbf{O})) &= \frac{42}{35}\pi^2, \\
\int_{\text{SO}(3)} d\mathbf{O} f_F(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_S(\mathbf{O})) &= -\frac{6}{35}\pi^2, \\
\int_{\text{SO}(3)} d\mathbf{O} f_F(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_U(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_F(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_P(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_F(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_F(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} f_{\psi_1}(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} f_S(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} f_U(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} f_P(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} f_F(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_S(\mathbf{O}) \nabla_{\mathbf{O}} f_{\psi_1}(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_S(\mathbf{O}) \nabla_{\mathbf{O}} f_S(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_S(\mathbf{O}) \nabla_{\mathbf{O}} f_U(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_S(\mathbf{O}) \nabla_{\mathbf{O}} f_P(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_S(\mathbf{O}) \nabla_{\mathbf{O}} f_F(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_U(\mathbf{O}) \nabla_{\mathbf{O}} f_{\psi_1}(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_U(\mathbf{O}) \nabla_{\mathbf{O}} f_{\psi_1}(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_U(\mathbf{O}) \nabla_{\mathbf{O}} f_U(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_U(\mathbf{O}) \nabla_{\mathbf{O}} f_P(\mathbf{O})) &= 0,
\end{aligned}$$

$$\begin{aligned}
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_U(\mathbf{O}) \nabla_{\mathbf{O}} f_F(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_P(\mathbf{O}) \nabla_{\mathbf{O}} f_{\psi_1}(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_P(\mathbf{O}) \nabla_{\mathbf{O}} f_S(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_P(\mathbf{O}) \nabla_{\mathbf{O}} f_U(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_P(\mathbf{O}) \nabla_{\mathbf{O}} f_P(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_P(\mathbf{O}) \nabla_{\mathbf{O}} f_F(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_{\psi_1}(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_S(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_U(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_P(\mathbf{O})) &= 0, \\
\int_{\text{SO}(3)} d\mathbf{O} f_{\psi_1}(\mathbf{O}) \nabla_{\mathbf{O}} \cdot (f_F(\mathbf{O}) \nabla_{\mathbf{O}} f_F(\mathbf{O})) &= 0.
\end{aligned}$$

APPENDIX B: COEFFICIENTS FOR MODEL 2

As with Model 1, here we evaluate the integrals required for calculating the coefficients in Eq. (85).

1. Translational diffusion

We first calculate all integrals of the form $\int d\mathbf{O} \frac{3}{2}(m_{3,i}m_{3,j} - \frac{1}{3})m_{3,k}m_{3,l} \mathbf{m}_3 \otimes \mathbf{m}_3$. Those are necessary to calculate the coefficients for translational diffusion:

$$\begin{aligned}
\int_{S_2} d\mathbf{O} m_{3,1}m_{3,1} \frac{3}{2} \left(m_{3,1}m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
= \begin{pmatrix} 16\pi/35 & 0 & 0 \\ 0 & 4\pi/105 & 0 \\ 0 & 0 & 4\pi/105 \end{pmatrix}, \\
\int_{S_2} d\mathbf{O} m_{3,1}m_{3,1} \frac{3}{2} \left(m_{3,1}m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
= \begin{pmatrix} -2\pi/5 & 6\pi/15 & 0 \\ 6\pi/15 & -2\pi/15 & 0 \\ 0 & 0 & -2\pi/15 \end{pmatrix}, \\
\int_{S_2} d\mathbf{O} m_{3,1}m_{3,1} \frac{3}{2} \left(m_{3,1}m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
= \begin{pmatrix} -2\pi/5 & 0 & 6\pi/35 \\ 0 & -2\pi/15 & 0 \\ 6\pi/15 & 0 & -2\pi/15 \end{pmatrix},
\end{aligned}$$

$$\begin{aligned}
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,1} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/5 & 0 & 0 \\ 0 & -2\pi/15 & 2\pi/35 \\ 0 & 2\pi/35 & -2\pi/15 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,1} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -8\pi/35 & 0 & 0 \\ 0 & 4\pi/105 & 0 \\ 0 & 0 & -8\pi/105 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,1} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -8\pi/35 & 0 & 0 \\ 0 & -8\pi/105 & 0 \\ 0 & 0 & 4\pi/105 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,2} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 4\pi/105 & 0 \\ 4\pi/105 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,2} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 6\pi/35 & -2\pi/15 & 0 \\ -2\pi/15 & 6\pi/15 & 0 \\ 0 & 0 & 2\pi/35 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,2} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & -2\pi/15 & 0 \\ -2\pi/15 & 0 & 2\pi/35 \\ 0 & 2\pi/35 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,2} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & -2\pi/15 & 2\pi/35 \\ -2\pi/15 & 0 & 0 \\ 2\pi/35 & 0 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,2} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 4\pi/105 & 0 \\ 4\pi/105 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,2} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & -8\pi/105 & 0 \\ -8\pi/105 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},
\end{aligned}$$

$$\begin{aligned}
& \int_{S_2} d\mathbf{O} m_{3,1} \mathbf{m}_3, \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 0 & 4\pi/105 \\ 0 & 0 & 0 \\ 4\pi/105 & 0 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,3} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 0 & -2\pi/15 \\ 0 & 0 & 2\pi/35 \\ -2\pi/15 & 2\pi/35 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,3} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 6\pi/35 & 0 & -2\pi/15 \\ 0 & 2\pi/35 & 0 \\ -2\pi/15 & 0 & 6\pi/15 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,3} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 2\pi/35 & -2\pi/15 \\ 2\pi/35 & 0 & 0 \\ -2\pi/15 & 0 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,3} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 0 & -8\pi/105 \\ 0 & 0 & 0 \\ -8\pi/105 & 0 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,1} m_{3,3} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 0 & 4\pi/105 \\ 0 & 0 & 0 \\ 4\pi/105 & 0 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,3} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -8\pi/105 \\ 0 & -8\pi/105 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,3} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 0 & 2\pi/35 \\ 0 & 0 & -2\pi/15 \\ 2\pi/35 & -2\pi/15 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,3} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 2\pi/35 & 0 \\ 2\pi/35 & 0 & -2\pi/15 \\ 0 & -2\pi/15 & 0 \end{pmatrix},
\end{aligned}$$

$$\begin{aligned}
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,3} \frac{3}{2} \left(m_{3,2} m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 2\pi/35 & 0 & 0 \\ 0 & 6\pi/35 & -2\pi/15 \\ 0 & -2\pi/15 & 6\pi/35 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,3} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 4\pi/105 \\ 0 & 4\pi/105 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,3} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 4\pi/105 \\ 0 & 4\pi/105 & 0 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,2} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 4\pi/105 & 0 & 0 \\ 0 & -8\pi/35 & 0 \\ 0 & 0 & -8\pi/105 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,2} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/15 & 6\pi/35 & 0 \\ 6\pi/35 & -2\pi/5 & 0 \\ 0 & 0 & -2\pi/15 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,2} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/15 & 0 & 2\pi/35 \\ 0 & -2\pi/5 & 0 \\ 2\pi/35 & 0 & -2\pi/15 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,2} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/15 & 0 & 0 \\ 0 & -2\pi/5 & 6\pi/35 \\ 0 & 6\pi/35 & -2\pi/15 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,2} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/15 & 0 & 0 \\ 0 & -2\pi/5 & 6\pi/35 \\ 0 & 6\pi/35 & -2\pi/15 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,2} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 4\pi/105 & 0 & 0 \\ 0 & 16\pi/35 & 0 \\ 0 & 0 & 4\pi/105 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,2} m_{3,2} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -8\pi/105 & 0 & 0 \\ 0 & -8\pi/35 & 0 \\ 0 & 0 & 4\pi/105 \end{pmatrix},
\end{aligned}$$

$$\begin{aligned}
& \int_{S_2} d\mathbf{O} m_{3,3} m_{3,3} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 4\pi/105 & 0 & 0 \\ 0 & -8\pi/105 & 0 \\ 0 & 0 & -8\pi/35 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,3} m_{3,3} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/15 & 2\pi/35 & 0 \\ 2\pi/35 & -2\pi/15 & 0 \\ 0 & 0 & -2\pi/5 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,3} m_{3,3} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/15 & 0 & 6\pi/35 \\ 0 & -2\pi/15 & 0 \\ 6\pi/35 & 0 & -2\pi/5 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,3} m_{3,3} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/15 & 0 & 0 \\ 0 & -2\pi/15 & 6\pi/35 \\ 0 & 6\pi/35 & -2\pi/5 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,3} m_{3,3} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -8\pi/105 & 0 & 0 \\ 0 & 4\pi/105 & 0 \\ 0 & 0 & -8\pi/35 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} m_{3,3} m_{3,3} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 4\pi/105 & 0 & 0 \\ 0 & 4\pi/105 & 0 \\ 0 & 0 & 16\pi/35 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} 8\pi/15 & 0 & 0 \\ 0 & 4\pi/15 & 0 \\ 0 & 0 & 4\pi/15 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/3 & 2\pi/5 & 0 \\ 2\pi/5 & -2\pi/3 & 0 \\ 0 & 0 & -2\pi/3 \end{pmatrix}, \\
& \int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3 \\
&= \begin{pmatrix} -2\pi/3 & 0 & 2\pi/5 \\ 0 & -2\pi/3 & 0 \\ 2\pi/5 & 0 & -2\pi/3 \end{pmatrix},
\end{aligned}$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3$$

$$= \begin{pmatrix} -2\pi/3 & 0 & 0 \\ 0 & -2\pi/3 & 2\pi/5 \\ 0 & 2\pi/5 & -2\pi/3 \end{pmatrix},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3$$

$$= \begin{pmatrix} 4\pi/15 & 0 & 0 \\ 0 & 8\pi/15 & 0 \\ 0 & 0 & 4\pi/15 \end{pmatrix},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \mathbf{m}_3 \otimes \mathbf{m}_3$$

$$= \begin{pmatrix} -4\pi/15 & 0 & 0 \\ 0 & -4\pi/15 & 0 \\ 0 & 0 & 8\pi/15 \end{pmatrix}.$$

Finally, we calculate all integrals of the form $\int d\mathbf{O} m_{3,k} m_{3,l} \mathbf{m}_3 \otimes \mathbf{m}_3$:

$$\int_{S_2} d\mathbf{O} \mathbf{m}_3 \otimes \mathbf{m}_3 = \begin{pmatrix} 4\pi/3 & 0 & 0 \\ 0 & 4\pi/3 & 0 \\ 0 & 0 & 4\pi/3 \end{pmatrix},$$

$$\int_{S_2} d\mathbf{O} m_{3,1} m_{3,1} \mathbf{m}_3 \otimes \mathbf{m}_3 = \begin{pmatrix} 4\pi/5 & 0 & 0 \\ 0 & 4\pi/15 & 0 \\ 0 & 0 & 4\pi/15 \end{pmatrix},$$

$$\int_{S_2} d\mathbf{O} m_{3,2} m_{3,2} \mathbf{m}_3 \otimes \mathbf{m}_3 = \begin{pmatrix} 4\pi/15 & 0 & 0 \\ 0 & 4\pi/5 & 0 \\ 0 & 0 & 4\pi/15 \end{pmatrix},$$

$$\int_{S_2} d\mathbf{O} m_{3,3} m_{3,3} \mathbf{m}_3 \otimes \mathbf{m}_3 = \begin{pmatrix} 4\pi/15 & 0 & 0 \\ 0 & 4\pi/15 & 0 \\ 0 & 0 & 4\pi/5 \end{pmatrix},$$

$$\int_{S_2} d\mathbf{O} m_{3,1} m_{3,2} \mathbf{m}_3 \otimes \mathbf{m}_3 = \begin{pmatrix} 0 & 4\pi/15 & 0 \\ 4\pi/15 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\int_{S_2} d\mathbf{O} m_{3,1} m_{3,3} \mathbf{m}_3 \otimes \mathbf{m}_3 = \begin{pmatrix} 0 & 0 & 4\pi/15 \\ 0 & 0 & 0 \\ 4\pi/15 & 0 & 0 \end{pmatrix},$$

$$\int_{S_2} d\mathbf{O} m_{3,2} m_{3,3} \mathbf{m}_3 \otimes \mathbf{m}_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 4\pi/15 \\ 0 & 4\pi/15 & 0 \end{pmatrix}.$$

2. Rotational diffusion

Now, we need to calculate the coefficients for the rotational diffusion. We start with the integrals of the form $\int_{S_2} d\mathbf{O} \nabla_{\mathbf{O}}^2 u_i u_k$:

$$\int_{S_2} d\mathbf{O} \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,1} = -\frac{8\pi}{3},$$

$$\int_{S_2} d\mathbf{O} \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,2} = -\frac{8\pi}{3},$$

$$\int_{S_2} d\mathbf{O} \nabla_{\mathbf{O}}^2 m_{3,3} m_{3,3} = \frac{16\pi}{3},$$

$$\int_{S_2} d\mathbf{O} \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,2} = 0,$$

$$\int_{S_2} d\mathbf{O} \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,3} = 0,$$

$$\int_{S_2} d\mathbf{O} \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,3} = 0.$$

Now we move on to all integrals of the form $\int_{S_2} d\mathbf{O} \frac{3}{2} (m_{3,k} m_{3,l} - \frac{1}{3}) \nabla_{\mathbf{O}}^2 u_i u_j$:

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,1} = -\frac{46\pi}{15},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,2} = 0,$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,3} = 0,$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,3} = 0,$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,2} = \frac{38\pi}{15},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,1} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,3} m_{3,3} = \frac{8\pi}{15},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,1} = \frac{4\pi}{3},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,2} = -\frac{14\pi}{5},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,3} = 0,$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,3} = 0,$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,2} = \frac{4\pi}{3},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,3} m_{3,3} = -\frac{8\pi}{3},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,1} = \frac{4\pi}{3},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,2} = 0,$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,3} = -\frac{14\pi}{5},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,3} = 0,$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,2} = \frac{4\pi}{3},$$

$$\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,1} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,3} m_{3,3} = -\frac{8\pi}{3},$$

$$\begin{aligned}
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,1} &= \frac{4\pi}{3}, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,2} &= 0, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,3} &= 0, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,3} &= -\frac{14\pi}{5}, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,2} &= \frac{4\pi}{3}, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,3} m_{3,3} &= -\frac{8\pi}{3}, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,1} &= \frac{38\pi}{15}, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,2} &= 0, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,3} &= 0,
\end{aligned}$$

$$\begin{aligned}
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,3} &= 0, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,2} &= -\frac{46\pi}{15}, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,2} m_{3,2} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,3} m_{3,3} &= \frac{8\pi}{15}, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,1} &= \frac{8\pi}{15}, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,2} &= 0, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,1} m_{3,3} &= 0, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,3} &= 0, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,2} m_{3,2} &= \frac{8\pi}{15}, \\
\int_{S_2} d\mathbf{O} \frac{3}{2} \left(m_{3,3} m_{3,3} - \frac{1}{3} \right) \nabla_{\mathbf{O}}^2 m_{3,3} m_{3,3} &= -\frac{16\pi}{15}.
\end{aligned}$$

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- [1] P.-G. De Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, Oxford, 1993).
- [2] S. Dussi and M. Dijkstra, Entropy-driven formation of chiral nematic phases by computer simulations, *Nat. Commun.* **7**, 11175 (2016).
- [3] L. Tran, M. O. Lavrentovich, D. A. Beller, N. Li, K. J. Stebe, and R. D. Kamien, Lassoing saddle splay and the geometrical control of topological defects, *Proc. Natl. Acad. Sci. USA* **113**, 7106 (2016).
- [4] M. Chiappini, T. Drwenski, R. van Roij, and M. Dijkstra, Biaxial, twist-bend, and splay-bend nematic phases of banana-shaped particles revealed by lifting the smectic blanket, *Phys. Rev. Lett.* **123**, 068001 (2019).
- [5] G. De Matteis, L. Martina, C. Naya, and V. Turco, Skyrmion tubes in achiral nematic liquid crystals, *Phys. Rev. E* **105**, 024701 (2022).
- [6] O. D. Lavrentovich, Ferroelectric nematic liquid crystal, a century in waiting, *Proc. Natl. Acad. Sci. USA* **117**, 14629 (2020).
- [7] F. Caimi, G. Nava, S. Fuschetto, L. Lucchetti, P. Paiè, R. Osellame, X. Chen, N. A. Clark, M. A. Glaser, and T. Bellini, Fluid superscreening and polarization following in confined ferroelectric nematics, *Nat. Phys.* **19**, 1658 (2023).
- [8] B. Zappone, A. E. Mamuk, I. Gryn, V. Arima, A. Zizzari, R. Bartolino, E. Lacaze, and R. Petschek, Analogy between periodic patterns in thin smectic liquid crystal films and the intermediate state of superconductors, *Proc. Natl. Acad. Sci. USA* **117**, 17643 (2020).
- [9] J. Xia, S. MacLachlan, T. J. Atherton, and P. E. Farrell, Structural landscapes in geometrically frustrated smectics, *Phys. Rev. Lett.* **126**, 177801 (2021).
- [10] J. Paget, M. G. Mazza, A. J. Archer, and T. N. Shendruk, Complex-tensor theory of simple smectics, *Nat. Commun.* **14**, 1048 (2023).
- [11] E. I. Jull, G. Campos-Villalobos, Q. Tang, M. Dijkstra, and L. Tran, Curvature-directed anchoring and defect structure of colloidal smectic liquid crystals in confinement, *PNAS Nexus* **3**, 470 (2024).
- [12] A. Doostmohammadi, J. Ignés-Mullol, J. M. Yeomans, and F. Sagués, Active nematics, *Nat. Commun.* **9**, 3246 (2018).
- [13] Z.-F. Huang, H. Löwen, and A. Voigt, Defect dynamics in active smectics induced by confining geometry and topology, *Commun. Phys.* **5**, 294 (2022).
- [14] F. Jülicher, J. Prost, and J. Toner, Broken living layers: Dislocations in active smectic liquid crystals, *Phys. Rev. E* **106**, 054607 (2022).
- [15] G. J. Vroege and H. N. W. Lekkerkerker, Phase transitions in lyotropic colloidal and polymer liquid crystals, *Rep. Prog. Phys.* **55**, 1241 (1992).
- [16] S. Singh, Phase transitions in liquid crystals, *Phys. Rep.* **324**, 107 (2000).
- [17] J. P. F. Lagerwall and G. Scalia, A new era for liquid crystal research: Applications of liquid crystals in soft matter nano-, bio- and microtechnology, *Curr. Appl. Phys.* **12**, 1387 (2012).
- [18] J. Uchida, B. Soberats, M. Gupta, and T. Kato, Advanced functional liquid crystals, *Adv. Mater.* **34**, 2109063 (2022).
- [19] *Biaxial Nematic Liquid Crystals: Theory, Simulation and Experiment*, edited by G. R. Luckhurst and T. J. Sluckin (Wiley, Chichester, UK, 2015).
- [20] M. J. Freiser, Ordered states of a nematic liquid, *Phys. Rev. Lett.* **24**, 1041 (1970).

- [21] R. Alben, Phase transitions in a fluid of biaxial particles, *Phys. Rev. Lett.* **30**, 778 (1973).
- [22] M. P. Taylor and J. Herzfeld, Nematic and smectic order in a fluid of biaxial hard particles, *Phys. Rev. A* **44**, 3742 (1991).
- [23] A. G. Vanakaras, M. A. Bates, and D. J. Photinos, Theory and simulation of biaxial nematic and orthogonal smectic phases formed by mixtures of board-like molecules, *Phys. Chem. Chem. Phys.* **5**, 3700 (2003).
- [24] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Thermotropic biaxial nematic liquid crystals, *Phys. Rev. Lett.* **92**, 145505 (2004).
- [25] E. van den Pol, A. V. Petukhov, D. M. E. Thies-Weesie, D. V. Byelov, and G. J. Vroege, Experimental realization of biaxial liquid crystal phases in colloidal dispersions of boardlike particles, *Phys. Rev. Lett.* **103**, 258301 (2009).
- [26] Y. Martínez-Ratón, S. Varga, and E. Velasco, Biaxial nematic phases in fluids of hard board-like particles, *Phys. Chem. Chem. Phys.* **13**, 13247 (2011).
- [27] S. Belli, A. Patti, M. Dijkstra, and R. van Roij, Polydispersity stabilizes biaxial nematic liquid crystals, *Phys. Rev. Lett.* **107**, 148303 (2011).
- [28] S. D. Peroukidis and A. G. Vanakaras, Phase diagram of hard board-like colloids from computer simulations, *Soft Matter* **9**, 7419 (2013).
- [29] A. B. G. M. Leferink op Reinink, S. Belli, R. Van Roij, M. Dijkstra, A. V. Petukhov, and G. J. Vroege, Tuning biaxiality of nematic phases of board-like colloids by an external magnetic field, *Soft Matter* **10**, 446 (2014).
- [30] A. Cuetos, M. Dennison, A. Masters, and A. Patti, Phase behaviour of hard board-like particles, *Soft Matter* **13**, 4720 (2017).
- [31] A. El Moumane, M. te Vrugt, H. Löwen, and R. Wittmann, Biaxial nematic order in fundamental measure theory, *J. Chem. Phys.* **160**, 094903 (2024).
- [32] A. Kuijk, A. Van Blaaderen, and A. Imhof, Synthesis of monodisperse, rodlike silica colloids with tunable aspect ratio, *J. Am. Chem. Soc.* **133**, 2346 (2011).
- [33] Q. Yu, K. Wang, J. Zhang, M. Liu, Y. Liu, and C. Cheng, Synthesis of anisotropic silica colloids, *RSC Adv.* **7**, 37542 (2017).
- [34] C. Chen, L. Xie, and Y. Wang, Recent advances in the synthesis and applications of anisotropic carbon and silica-based nanoparticles, *Nano Res.* **12**, 1267 (2019).
- [35] R. Evans, The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids, *Adv. Phys.* **28**, 143 (1979).
- [36] U. Marini Bettolo Marconi and P. Tarazona, Dynamic density functional theory of fluids, *J. Chem. Phys.* **110**, 8032 (1999).
- [37] A. J. Archer and R. Evans, Dynamical density functional theory and its application to spinodal decomposition, *J. Chem. Phys.* **121**, 4246 (2004).
- [38] M. te Vrugt, H. Löwen, and R. Wittkowski, Classical dynamical density functional theory: From fundamentals to applications, *Adv. Phys.* **69**, 121 (2020).
- [39] M. te Vrugt and R. Wittkowski, Perspective: New directions in dynamical density functional theory, *J. Phys.: Condens. Matter* **35**, 041501 (2023).
- [40] A. Chandra and B. Bagchi, Molecular theory of solvation and solvation dynamics of a classical ion in a dipolar liquid, *J. Phys. Chem.* **93**, 6996 (1989).
- [41] G. V. Vijayadamodar, A. Chandra, and B. Bagchi, Effects of translational diffusion on dielectric friction in a dipolar liquid, *Chem. Phys. Lett.* **161**, 413 (1989).
- [42] A. Chandra and B. Bagchi, Collective orientational relaxation in a dense liquid of ellipsoidal molecules, *Physica A* **169**, 246 (1990).
- [43] B. Bagchi and A. Chandra, Molecular theory of underdamped dielectric relaxation: Understanding collective effects in dipolar liquids, *Chem. Phys.* **173**, 133 (1993).
- [44] A. Chandra and B. Bagchi, The role of translational diffusion in the polarization relaxation in dense polar liquids, *Chem. Phys. Lett.* **151**, 47 (1988).
- [45] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids: Fundamentals*, 1st ed., International Series of Monographs on Chemistry 9 (Oxford University Press, Oxford, 1984), Vol. 1, p. 626.
- [46] R. Wittkowski and H. Löwen, Dynamical density functional theory for colloidal particles with arbitrary shape, *Mol. Phys.* **109**, 2935 (2011).
- [47] M. A. Durán-Olivencia, P. Yatsyshin, B. D. Goddard, and S. Kalliadasis, General framework for fluctuating dynamic density functional theory, *New J. Phys.* **19**, 123022 (2017).
- [48] M. Bier, R. van Roij, M. Dijkstra, and P. van der Schoot, Self-diffusion of particles in complex fluids: Temporary cages and permanent barriers, *Phys. Rev. Lett.* **101**, 215901 (2008).
- [49] M. Klopotek, H. Hansen-Guus, M. Dixit, T. Schilling, F. Schreiber, and M. Oettel, Monolayers of hard rods on planar substrates. II. Growth, *J. Chem. Phys.* **146**, 084903 (2017).
- [50] S. Mondal, S. Mukherjee, and B. Bagchi, Origin of diverse time scales in the protein hydration layer solvation dynamics: A simulation study, *J. Chem. Phys.* **147**, 154901 (2017).
- [51] H. H. Wensink and H. Löwen, Aggregation of self-propelled colloidal rods near confining walls, *Phys. Rev. E* **78**, 031409 (2008).
- [52] M. te Vrugt, M. P. Holl, A. Koch, R. Wittkowski, and U. Thiele, Derivation and analysis of a phase field crystal model for a mixture of active and passive particles, *Model. Simul. Mater. Sci. Eng.* **30**, 084001 (2022).
- [53] K. R. Elder, M. Katakowski, M. Haataja, and M. Grant, Modeling elasticity in crystal growth, *Phys. Rev. Lett.* **88**, 245701 (2002).
- [54] H. Emmerich, H. Löwen, R. Wittkowski, T. Gruhn, G. I. Tóth, G. Tegze, and L. Gránásy, Phase-field-crystal models for condensed matter dynamics on atomic length and diffusive time scales: An overview, *Adv. Phys.* **61**, 665 (2012).
- [55] K. R. Elder, N. Provatas, J. Berry, P. Stefanovic, and M. Grant, Phase-field crystal modeling and classical density functional theory of freezing, *Phys. Rev. B* **75**, 064107 (2007).
- [56] S. van Teeffelen, R. Backofen, A. Voigt, and H. Löwen, Derivation of the phase-field-crystal model for colloidal solidification, *Phys. Rev. E* **79**, 051404 (2009).
- [57] A. J. Archer, D. J. Ratliff, A. M. Rucklidge, and P. Subramanian, Deriving phase field crystal theory from dynamical density functional theory: Consequences of the approximations, *Phys. Rev. E* **100**, 022140 (2019).
- [58] H. Löwen, A phase-field-crystal model for liquid crystals, *J. Phys.: Condens. Matter* **22**, 364105 (2010).
- [59] R. Wittkowski, H. Löwen, and H. R. Brand, Derivation of a three-dimensional phase-field-crystal model for liquid crystals from density functional theory, *Phys. Rev. E* **82**, 031708 (2010).

- [60] R. Wittkowski, H. Löwen, and H. R. Brand, Polar liquid crystals in two spatial dimensions: The bridge from microscopic to macroscopic modeling, *Phys. Rev. E* **83**, 061706 (2011).
- [61] R. Wittkowski, H. Löwen, and H. R. Brand, Microscopic and macroscopic theories for the dynamics of polar liquid crystals, *Phys. Rev. E* **84**, 041708 (2011).
- [62] A. M. Menzel and H. Löwen, Traveling and resting crystals in active systems, *Phys. Rev. Lett.* **110**, 055702 (2013).
- [63] A. M. Menzel, T. Ohta, and H. Löwen, Active crystals and their stability, *Phys. Rev. E* **89**, 022301 (2014).
- [64] L. Ophaus, S. V. Gurevich, and U. Thiele, Resting and traveling localized states in an active phase-field-crystal model, *Phys. Rev. E* **98**, 022608 (2018).
- [65] M. te Vrugt, J. Jeggle, and R. Wittkowski, Jerky active matter: A phase field crystal model with translational and orientational memory, *New J. Phys.* **23**, 063023 (2021).
- [66] T. Frohoff-Hülsmann, M. P. Holl, E. Knobloch, S. V. Gurevich, and U. Thiele, Stationary broken parity states in active matter models, *Phys. Rev. E* **107**, 064210 (2023).
- [67] M. te Vrugt, J. Jeggle, and R. Wittkowski, Passive and active field theories for disease spreading, *J. Phys. A* **57**, 315003 (2024).
- [68] Z.-F. Huang, A. M. Menzel, and H. Löwen, Dynamical crystallites of active chiral particles, *Phys. Rev. Lett.* **125**, 218002 (2020).
- [69] D. Arold and M. Schmiedeberg, Active phase field crystal systems with inertial delay and underdamped dynamics, *Eur. Phys. J. E* **43**, 47 (2020).
- [70] M. P. Holl, A. J. Archer, S. V. Gurevich, E. Knobloch, L. Ophaus, and U. Thiele, Localized states in passive and active phase-field-crystal models, *IMA J. Appl. Math.* **86**, 896 (2021).
- [71] R. F. B. Weigel and M. Schmiedeberg, Phase field crystal model for particles with n -fold rotational symmetry in two dimensions, *Model. Simul. Mater. Sci. Eng.* **30**, 074003 (2022).
- [72] J. Bickmann, Collective Dynamics of Active Brownian Particle Systems, Ph.D. thesis, University of Münster (2022).
- [73] R. Rosso, Orientational order parameters in biaxial nematics: Polymorphic notation, *Liq. Cryst.* **34**, 737 (2007).
- [74] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
- [75] R. Roth, Fundamental measure theory for hard-sphere mixtures: A review, *J. Phys.: Condens. Matter* **22**, 063102 (2010).
- [76] T. V. Ramakrishnan and M. Yussouff, First-principles order-parameter theory of freezing, *Phys. Rev. B* **19**, 2775 (1979).
- [77] L. Onsager, The effects of shape on the interaction of colloidal particles, *Ann. N.Y. Acad. Sci.* **51**, 627 (1949).
- [78] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids: With Applications to Soft Matter* (Academic Press, Oxford, 2009).
- [79] S. M. Tschopp and J. M. Brader, First-principles superadiabatic theory for the dynamics of inhomogeneous fluids, *J. Chem. Phys.* **157**, 234108 (2022).
- [80] S. S. Turzi, On the Cartesian definition of orientational order parameters, *J. Math. Phys.* **52**, 053517 (2011).
- [81] L. Longa, P. Grzybowski, S. Romano, and E. Virga, Minimal coupling of the biaxial nematic phase, *Phys. Rev. E* **71**, 051714 (2005).
- [82] M. te Vrugt and R. Wittkowski, Relations between angular and Cartesian orientational expansions, *AIP Adv.* **10**, 035106 (2020).
- [83] D. Topgaard, Director orientations in lyotropic liquid crystals: Diffusion MRI mapping of the Saupe order tensor, *Phys. Chem. Chem. Phys.* **18**, 8545 (2016).
- [84] M. te Vrugt and R. Wittkowski, Orientational order parameters for arbitrary quantum systems, *Ann. Phys. (Berlin)* **532**, 2000266 (2020).
- [85] J. Bickmann and R. Wittkowski, Collective dynamics of active Brownian particles in three spatial dimensions: A predictive field theory, *Phys. Rev. Res.* **2**, 033241 (2020).
- [86] B. Mulder, Isotropic-symmetry-breaking bifurcations in a class of liquid-crystal models, *Phys. Rev. A* **39**, 360 (1989).
- [87] N. J. Mottram and C. J. P. Newton, Introduction to Q-tensor theory, [arXiv:1409.3542](https://arxiv.org/abs/1409.3542).
- [88] A. Simon, J. Weimar, G. Martius, and M. Oettel, Machine learning of a density functional for anisotropic patchy particles, *J. Chem. Theory Comput.* **20**, 1062 (2024).
- [89] G. De Matteis, Continuum Landau model for biaxial nematic liquid crystals, *Mol. Cryst. Liq. Cryst.* **500**, 31 (2009).
- [90] G. De Matteis, A. M. Sonnet, and E. G. Virga, Landau theory for biaxial nematic liquid crystals with two order parameter tensors, *Continuum. Mech. Thermodyn.* **20**, 347 (2008).
- [91] J. Xu and J. Z. Y. Chen, General liquid-crystal theory for anisotropically shaped molecules: Symmetry, orientational order parameters, and system free energy, *Phys. Rev. E* **102**, 062701 (2020).
- [92] L. Longa, D. Monselesan, and H.-R. Trebin, An extension of the Landau-Ginzburg-de Gennes theory for liquid crystals, *Liq. Cryst.* **2**, 769 (1987).
- [93] L. Longa and H.-R. Trebin, Structure of the elastic free energy for chiral nematic liquid crystals, *Phys. Rev. A* **39**, 2160 (1989).
- [94] R. Wittmann, *Density Functional Theory for Liquid Crystals: Refining Fundamental Measure Theory for Anisotropic Bodies* (FAU University Press, Erlangen, 2015).
- [95] S.-C. Lin, M. Oettel, J. M. Häring, R. Haussmann, M. Fuchs, and G. Kahl, Direct correlation function of a crystalline solid, *Phys. Rev. Lett.* **127**, 085501 (2021).
- [96] H. Graf and H. Löwen, Density functional theory for hard spherocylinders: Phase transitions in the bulk and in the presence of external fields, *J. Phys.: Condens. Matter* **11**, 1435 (1999).
- [97] J. K. G. Dhont, *An Introduction to Dynamics of Colloids*, 1st ed., Studies in Interface Science (Elsevier, Amsterdam, 1996), Vol. 2.
- [98] S. Yabunaka and T. Araki, Polydomain growth at isotropic-nematic transitions in liquid crystalline polymers, *Phys. Rev. E* **83**, 061711 (2011).
- [99] A. El Moumane, R. Wittmann, H. Löwen, and M. te Vrugt, Supplementary Data ([Zenodo, Dataset](https://zenodo.org/record/1511111), 2025). The content of this dataset corresponds to the content of Appendices A and B of this article.