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Enhanced Landau–de Gennes potential for nematic liquid crystals from a systematic coarse-graining procedure

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The macroscopic theory of nematics is conveniently described in terms of the phenomenological Landau–de Gennes free energy. Here we show how such an effective free energy can be obtained explicitly from a microscopic model via the help of a systematic coarse-graining procedure. We test our approach for the two- and three-dimensional Lebwohl-Lasher model of nematics. The effective free energy that we obtain is consistent with the phenomenological Landau–de Gennes form for weak orientational ordering and the Maier-Saupe theory of the isotropic-nematic transition. For strong orientational ordering, however, the effective free energy increases rapidly and diverges logarithmically near the fully oriented state. The explicit form for the regularized Landau–de Gennes potential proposed here restricts the order parameter to physical admissible values and reproduces our numerical data accurately.

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I. INTRODUCTION

Nematic liquid crystals undergo a first-order isotropic-to-nematic transition below a critical temperature or above a critical concentration, where orientational ordering spontaneously breaks rotational symmetry [1]. External electromagnetic or flow fields can reorient or induce their orientational order [2,3]. Therefore, liquid crystals are not only of great theoretical interest but also of significant practical use in displays, as well as for biological materials [4].

On a mean-field, macroscopic level, the system is conveniently described in terms of an orientational order parameter tensor $\mathbf{Q}$. Near the transition, de Gennes expanded the effective free energy $\mathcal{F}(\mathbf{Q})$ up to fourth order in the tensorial invariants of $\mathbf{Q}$, in analogy to the Ginzburg-Landau theory of phase transitions [1]. The resulting Landau–de Gennes free energy $\mathcal{F}$ is now very widely used, even for flowing nematics (see, e.g., Ref. [4,5] and references therein). From simulations of a molecular model, it was found that fluctuations lead to deviations from the Landau–de Gennes theory, especially close to the transition [6]. In addition, since the orientational order parameter is bounded, the validity of the fourth-order expansion breaks down far from the transition and also in nonequilibrium situations. This problem has already been noted several times in the literature [7–9] and led to the conclusion that the Landau–de Gennes theory "cannot make detailed quantitative predictions" [10]. Therefore, an empirical penalty function [7] or an amended potential [9,11] have been proposed in order to improve on the original Landau–de Gennes potential. The amended potential proposed in Ref. [9] was motivated by the mesoscopic Hess-Doi kinetic model [12,13]. Starting with Onsager's seminal work, different versions of density functional theories for the isotropic-nematic transition have been proposed and studied [14–17]. Alternatively, there have been some approaches for a microscopic foundation and derivation of the effective free energy $\mathcal{F}(\mathbf{Q})$ by field-theoretic methods [18,19]. Unfortunately these approaches have not led to an expression for $\mathcal{F}(\mathbf{Q})$ that is sufficiently simple in order to be useful for further theoretical or numerical studies.

Here we approach this old problem in the light of recent coarse-graining approaches that have been developed mainly for polymer dynamics [20]. An important prerequisite for a proper free energy is the choice of a corresponding, representative ensemble that is relevant on a macroscopic scale. Following common practice, we here choose the quasi-equilibrium or generalized canonical distribution. Then, we can interpret the effective free energy as the thermodynamic potential corresponding to this ensemble for given values of $\mathbf{Q}$. We test the approach for the two- and three-dimensional Lebwohl-Lasher model. We perform Monte Carlo simulations of this model in the generalized canonical ensemble and calculate numerically the effective free energy via thermodynamic integration. With Eq. (11) an analytic, nonpolynomial form of the effective free energy is proposed that describes the numerical values very accurately. This expression for the free energy can replace the usual Landau–de Gennes potential for an enhanced macroscopic description of nematics.

The paper is organized as follows: In Sec. II we describe the general approach to the effective free energy. In Sec. III we specify the general approach to the specific case of the Lebwohl-Lasher model. The mean-field free energy is derived in Sec. III A, and the numerical procedure described in Sec. III B. The numerical values from Monte Carlo simulations are compared to the predictions of the macroscopic free energy in Secs. III C–III F. Finally, as example applications, we discuss the field-induced orientation in Sec. III G. Some conclusions and outlook are presented in Sec. IV.

II. EFFECTIVE FREE ENERGY

The orientational ordering of nematics is described in terms of an order parameter tensor $\mathbf{Q}$, which is a symmetric, traceless second-rank tensor. In the vicinity of the transition, it is postulated that the system can be described in terms of a Landau–de Gennes free energy $L(\mathbf{Q})$ [1]. Frame invariance requires that L depends only on tensorial invariants of $\mathbf{Q}$. Since the order parameter is small at the transition, it is assumed that $L(\mathbf{Q})$ can be expanded as [1]

$$L(\mathbf{Q}) = \tfrac{1}{2}A\mathrm{tr}\{\mathbf{Q}\cdot\mathbf{Q}\} + \tfrac{1}{3}B\mathrm{tr}\{\mathbf{Q}\cdot\mathbf{Q}\cdot\mathbf{Q}\} + \tfrac{1}{4}C\mathrm{tr}\{\mathbf{Q}\cdot\mathbf{Q}\}^2. \tag{1}$$

In the Landau–de Gennes theory, the isotropic state looses its stability at the temperature T', which is easiest reflected in $A(T) = a(T - T')$. The coefficients B,C are considered as constants, where $B < 0$ is characteristic for first-order phase transitions and $C > 0$ ensures stability. When B and C are allowed to depend on temperature, an improved comparison with experimental results can be achieved [21].

The simplicity and universality of the Landau–de Gennes theory is remarkable and has led to its wide use in the theoretical description of nematics. On the other hand, the limitations of the Landau–de Gennes approach (1) are obvious and have been pointed out repeatedly in the literature. The validity of the fourth-order expansion is questionable even in the vicinity of the transition [6], let alone in nonequilibrium situations. Furthermore, the coefficients A,B, and C are phenomenological and lack a molecular interpretation. For these reasons, it would be highly desirable to a establish microscopic foundation of the Landau–de Gennes theory. Several attempts to achieve this have been done in the literature. One type of approach aimed at establishing a connection with the Maier-Saupe theory of nematics but essentially failed to do so [6]. More successful have been approaches using density functional theories [16,22]. It should be noted, however, that by their very nature these approaches deal with free energy functionals that are in general not easily expressed as Landau free energies in terms of the order parameter $\mathbf{Q}$ only.

Consider a microscopic model for a liquid crystal with Hamiltonian H at temperature T in canonical equilibrium. Formally, the Landau free energy can be defined via the restricted partition function $\exp[-\beta L(\mathbf{Q})] = \exp[-\beta F]\langle\delta(\mathbf{Q} - \mathbf{\Pi})\rangle$, $\beta = (k_{\mathrm{B}}T)^{-1}$ and F the thermodynamic free energy satisfying $\exp[-\beta F] = \int d\mathbf{Q}\, \exp[-\beta L(\mathbf{Q})]$ [23]. Averages with the canonical equilibrium distribution function ρ_0 are denoted by $\langle\bullet\rangle = \int d\Gamma\, \bullet\, \rho_0(\Gamma)$. The average is taken over all microscopic degrees of freedom Γ. The instantaneous order parameter tensor is defined by $\mathbf{\Pi} = N^{-1}\sum_j \overline{\mathbf{u}_j\mathbf{u}_j}$ with $\mathbf{Q} = \langle\mathbf{\Pi}\rangle$, and the three-dimensional unit vector $\mathbf{u}_j$ denotes the direction of rotationally symmetric particle j. We use the notation $\overline{\mathbf{a}} = (1/2)[\mathbf{a} + \mathbf{a}^T] - (1/3)\mathrm{tr}\{\mathbf{a}\}\mathbf{1}$ for the symmetric and traceless part of a tensor $\mathbf{a}$. The restricted partition function and the resulting effective potential became a frequently used concept in recent coarse-graining approaches [20], and several numerical methods for free energy calculations have been developed [24].

An alternative approach employs the generalized canonical distribution,

$$\rho_{\mathbf{\Lambda}}(\Gamma) = e^{-\beta H(\Gamma) - \mathbf{\Lambda}:\mathbf{\Pi}(\Gamma) + \beta G(\mathbf{\Lambda})}, \tag{2}$$

where only the average values of the chosen variables are fixed, $\mathbf{Q} = \langle\mathbf{\Pi}\rangle_{\mathbf{\Lambda}} = \int d\Gamma\, \rho_{\mathbf{\Lambda}}(\Gamma)\mathbf{\Pi}(\Gamma)$. For $\mathbf{\Lambda} = 0$, $\rho_{\mathbf{\Lambda}}$ reduces to the equilibrium distribution ρ_0. The generating function is defined by

$$e^{-\beta G(\mathbf{\Lambda})} = e^{-\beta G(0)}\langle e^{-\mathbf{\Lambda}:\mathbf{\Pi}}\rangle, \tag{3}$$

where the Lagrange multipliers $\mathbf{\Lambda}$ are the dual variables to $\mathbf{Q}$,

$$\mathbf{Q} = \frac{\partial(\beta G)}{\partial\mathbf{\Lambda}}. \tag{4}$$

From Eq. (2), one finds that the Lagrange multipliers as dual variables act as an orienting field conjugate to the order parameter. It is interesting to note that G and L are Laplace transforms of each other. However, the thermodynamic potential that corresponds to the generalized canonical ensemble is the Legendre transform of G,

$$\mathcal{F}(\mathbf{Q}) = G(\mathbf{\Lambda}(\mathbf{Q})) - k_{\mathrm{B}}T\,\mathbf{\Lambda}(\mathbf{Q}):\mathbf{Q}, \tag{5}$$

with $\partial\mathcal{F}/\partial\mathbf{Q} = -k_{\mathrm{B}}T\mathbf{\Lambda}$. Therefore, L and $\mathcal{F}$ are in general not equivalent. We note that L does not have a strict thermodynamic interpretation except as some coarse-grained free energy and is usually constructed phenomenologically [23].

In the following, we concentrate on the effective free energy $\mathcal{F}(\mathbf{Q})$, which is the proper thermodynamic potential for the chosen variables. The corresponding distribution (2) not only appears as the stationary distribution in the presence of an external magnetic or elongational flow field [25] but has been found to provide a good approximation in various nonequilibrium situations [26–28]. In addition, the generalized canonical ensemble is often employed in projection operator derivations of dynamical equations, where the gradient of $\mathcal{F}$ appear as driving forces [29]. For these reasons, $\mathcal{F}$ can be used within nonequilibrium thermodynamics to describe not only the statics but also the dynamics of liquid crystals [30].

For small deviations of $\mathbf{Q}$ from its equilibrium value, a cumulant expansion might be useful; see Sec. A. In order to make further progress, we resort to Monte Carlo simulations in the generalized canonical ensemble (2). The order parameter is then calculated as ensemble average $\mathbf{Q} = \langle\mathbf{\Pi}\rangle_{\mathbf{\Lambda}}$ for chosen values of $\mathbf{\Lambda}$. Inverting this relation yields $\mathbf{\Lambda}(\mathbf{Q})$, so that the effective free energy can then be obtained by thermodynamic integration

$$\mathcal{F}(\mathbf{Q}) = F - k_{\mathrm{B}}T\int_0^{\mathbf{Q}} \mathbf{\Lambda}(\mathbf{Q}') : d\mathbf{Q}', \tag{6}$$

where $F = \mathcal{F}(0)$ is the free energy in the equilibrium state (2) for $\mathbf{\Lambda} = 0$; see Eq. (A4). The final step is the reconstruction of a functional form of $\mathcal{F}(\mathbf{Q})$ that then can be used for further studies.

We have carried out a similar study very recently for the case of low-molecular polymer melts and thereby found an anharmonic entropic spring potential [31,32]. An important difference for the case of liquid crystals is the presence of the isotropic-nematic phase transition, which implies that the effective potential must differ significantly between high- and low-temperature phase, where it is no longer a convex function. Contrary to the case of flexible polymers, the entropic contribution to $\mathcal{F}$ from an ideal gas of orientational degrees of freedom is not trivial. We have worked out this contribution only very recently in Ref. [33].

III. LEBWOHL-LASHER MODEL

In order to test the approach outlined above, we apply the proposed algorithm to a simple lattice model of a nematic system proposed by Lebwohl and Lasher [34,35].

The Hamiltonian of the Lebwohl-Lasher model reads

$$H = -\frac{J}{2}\sum_{\langle i,j\rangle}\overline{\mathbf{u}_i\mathbf{u}_i} : \overline{\mathbf{u}_j\mathbf{u}_j}, \tag{7}$$

where $\langle i,j\rangle$ denote nearest neighbor pairs i and j on a given lattice. The spins $\mathbf{u}_j$ are allowed to rotate on the three-dimensional unit sphere, $\mathbf{u}_j^2 = 1$. The interaction energy between spins i and j can also be written as $-\epsilon P_2(\mathbf{u}_i \cdot \mathbf{u}_j)$, where $\epsilon = (2/3)J$ and $P_2(x) = (3x^2 - 1)/2$ denotes the second Legendre polynomial. In the planar Lebwohl-Lasher model, these spins are arranged on a two-dimensional square lattice, while a three-dimensional cubic lattice is employed for the three-dimensional model.

The model shows a weak first-order transition from an isotropic phase at high temperatures to a nematic state below a critical temperature, which according to recent finite-size scaling studies is around $k_B T_c/J \approx 0.37$ for the planar model on a square lattice [36]. In the three-dimensional case, the reduced transition temperature was estimated as $k_B T_c/J \approx 0.75$ for a simple cubic lattice [37,38], the numerical data being somewhat less accurate in this case.

A. Mean-field approximation

In the mean-field approximation, the Hamiltonian (7) is replaced by

$$H^{\mathrm{MFA}} = -\frac{1}{2} z J \sum_j \overline{\mathbf{u}_i \mathbf{u}_j} : \mathbf{Q}, \tag{8}$$

where z is the coordination number of the lattice, i.e., $z = 2D$ for a cubic lattice in D space dimensions. In Eq. (8) the sum over the neighboring spins in the original model (7) has been approximated by the average $\sum_{i\,\mathrm{nn}\,j} \overline{\mathbf{u}_i \mathbf{u}_i} \approx z\mathbf{Q}$, in analogy to the case of ferromagnets [23]. Then, the generating function G is given by Eq. (3) as $G(\mathbf{\Lambda}) = N G_{\mathrm{id}}(z\beta J \mathbf{Q} - \mathbf{\Lambda}/N)$, where $G_{\mathrm{id}}(\mathbf{A})$ is the generating function for the ideal, noninteracting system [33]. The mean-field approximation is identical to the saddle-point approximation of the corresponding field theory; see Appendix B. Using the results obtained in Ref. [33], we obtain an expression for the Lagrange multiplier $\mathbf{\Lambda}$ as a series expansion in the order parameter $\mathbf{Q}$. See Appendix C and in particular Eq. (C3) for details of the derivation.

Using the expression $\mathbf{\Lambda}(\mathbf{Q})$ from Eq. (C3) for thermodynamic integration (5), we obtain the mean-field expression for the effective free energy

$$\begin{aligned} \mathcal{F}^{\mathrm{MFA}}&(\mathbf{Q})/Nk_B T \\ &= f_0 + \frac{1}{2}\left(\frac{15}{2} - z\beta J\right)\mathrm{tr}\{\mathbf{Q}^2\} - \frac{75}{14}\mathrm{tr}\{\mathbf{Q}^3\} \\ &\quad + \frac{3825}{784}[\mathrm{tr}\{\mathbf{Q}^2\}]^2 + O(\mathbf{Q}^5) \end{aligned} \tag{9}$$

with $f_0 = F/Nk_B T$. Thus, the fourth-order expansion of the effective free energy is fully consistent with the classical Landau–de Gennes theory (1): Only the terms with correct tensorial structure appear in the expansion, and the coefficient A in Eq. (1) is given by $A(T)/N = \frac{15}{2} k_B (T - T')$, indeed, is proportional to $T - T'$ as was already found in Ref. [39] from pretransitional fluctuations. Finally, the coefficients B and C are constant with $B < 0$ and $C > 0$. Further support for the Landau–de Gennes theory comes from Monte Carlo simulations, where the effective free energy is obtained via Boltzmann inversion and shows the characteristic features of a weak first-order phase transition [38]. Within simplest mean-field approximation, the reduced temperatures where the isotropic state looses its stability are predicted as $k_B T'/J = 2z/15$, which is 0.53 and 0.8 for a simple cubic lattice in dimension $D = 2$ and $D = 3$, respectively.

By comparing Eq. (9) to the result of Ref. [33], one realizes that the effective free energy $\mathcal{F}^{\mathrm{MFA}}$ can be written as the sum of an entropic and a mean-field interaction term,

$$\mathcal{F}^{\mathrm{MFA}}(\mathbf{Q}) = E^{\mathrm{MFA}}(\mathbf{Q}) - T S^{\mathrm{id}}(\mathbf{Q}). \tag{10}$$

The entropy S^{id} is maximum for the isotropic state and decreases as the orientational ordering increases. In the spirit of the Lebwohl-Lasher model, S^{id} includes only the ideal entropy for the noninteracting system, while all interactions are energetic in nature. The mean-field interaction term is given by the average of the mean-field Hamiltonian, Eq. (8), $E^{\mathrm{MFA}} = \langle H^{\mathrm{MFA}} \rangle_{\mathbf{\Lambda}} = -\frac{1}{2} N z J \,\mathrm{tr}\{\mathbf{Q} \cdot \mathbf{Q}\}$. We therefore recover the characteristic features of the classical Maier-Saupe theory for the isotropic-nematic transition [1]. This is not surprising, since the Lebwohl-Lasher model was invented as a finite-dimensional, lattice version of the Maier-Saupe theory. Nevertheless, it is reassuring that the mean-field limit is correctly recovered within this procedure. For general and in particular off-lattice models, excluded volume interactions lead to an additional contribution to the entropy (see, e.g., Refs. [11,13,40] and references therein) that should be included in Eq. (10).

From our previous study [33], we know that S^{id} is not a low-order polynomial. When using the full expression for S^{id} in Eq. (10), we arrive at the following effective free energy, which is valid not only for weak but also for strong ordering:

$$\mathcal{F}(\mathbf{Q})/Nk_B T = -\tfrac{1}{2} z^* \beta J \,\mathrm{tr}\{\mathbf{Q} \cdot \mathbf{Q}\} - \ln(\sqrt{\mathcal{Q}}) - \tfrac{2}{3}(\sqrt{\mathcal{Q}} - 1), \tag{11}$$

where $\mathcal{Q} = 1 + 9(I_3 - I_2)$ with the tensorial invariants $I_2 = \frac{1}{2}\mathrm{tr}\{\mathbf{Q} \cdot \mathbf{Q}\}$ and $I_3 = \mathrm{tr}\{\mathbf{Q} \cdot \mathbf{Q} \cdot \mathbf{Q}\}$ ($I_1 = \mathrm{tr}\{\mathbf{Q}\} = 0$ by construction). We here introduce the effective coordination number z^* and allow for deviations from the mean-field value, which is 2D for D-dimensional simple cubic lattices. Equation (11) should be compared to the expansion (9) and also to the expression $\mathcal{F}^{\mathrm{D}}/Nk_B T = (1 - U/3)I_2 - \frac{U}{3} I_3 + U I_2^2$ proposed by Doi and Edwards in Ref. [13] and used frequently since then. The dimensionless interaction strength U can be related to the coupling strength J in the Lebwohl-Lasher model via the mean energy giving $U = (2/3) z^* \beta J$.

B. Numerical procedure

We want to test the theoretical predictions from mean-field theory against numerical simulations. To this end, we perform Monte Carlo simulations of the Lebwohl-Lasher model in the generalized canonical ensemble with Hamiltonian $\beta H' = \beta H - \mathbf{\Lambda} : \mathbf{\Pi}$, where $\mathbf{\Pi} = N^{-1} \sum_j \overline{\mathbf{u}_j \mathbf{u}_j}$. The standard Metropolis algorithm with random rotations of individual spins is employed with typically 5×10^6 Monte Carlo sweeps. Averages are extracted after a stationary state has been reached and error bars are estimated from block averages. For the planar model, we study systems with a square lattice of 50^2 sites with periodic boundary conditions. In addition, some studies are also performed with lattice sizes of 20^2 and 80^2 in order to estimate finite-size effects. As expected, system size effects are generally weak except near the phase transition. For the three-dimensional model, we mainly study a cubic lattice of size 20^3

with some simulations performed for a system with 30^3. Since the lattice geometry enters the macroscopic free energy (11) only via the effective coordination number z^*, we performed additional simulations on other two-dimensional lattices in order to study the universality of the macroscopic expression. These additional lattices are the honeycomb, semitriangular, and hexagonal lattice, which have coordination numbers 3,5, and 6, respectively. To the best of the author's knowledge, the Lebwohl-Lasher has so far not been studied on those lattices and therefore the corresponding critical temperature of the isotropic-nematic transition is unknown.

We use different choices for the Lagrange multipliers: $\mathbf{\Lambda} = N\lambda\overline{\mathbf{e}_z\mathbf{e}_z}$, and $\mathbf{\Lambda} = N\lambda(\mathbf{e}_x\mathbf{e}_x - \mathbf{e}_y\mathbf{e}_y)$, which corresponds to uniaxial and biaxial form, respectively, and $\mathbf{e}_\alpha$, $\alpha = x,y,z$ denote the unit vector parallel to the Cartesian axis. For each value of $\mathbf{\Lambda}$, we obtain the mean order parameter tensor $\mathbf{Q}(\mathbf{\Lambda})$ from Monte Carlo simulations after the equilibrium state has been reached. Error bars are estimated from block averages and are typically smaller than the symbols if not indicated otherwise.

C. Effective coordination number

Figure 1 shows the orientational order parameter for different temperatures. Increasing orientational order is obtained for increasing strength of the Lagrange multipliers, which act as an orienting field. The numerical data are well described by the relation

$$\mathbf{\Lambda}/N = z^*\beta J\mathbf{Q} + 9\left(\frac{1}{2Q} + \frac{1}{3\sqrt{Q}}\right)(3\overline{\mathbf{Q}.\mathbf{Q}} - \mathbf{Q}), \qquad (12)$$

obtained from $-k_BT\mathbf{\Lambda} = \partial\mathcal{F}/\partial\mathbf{Q}$, where the effective free energy is given by Eq. (11). For high temperatures $\beta J \to 0$, $\mathbf{Q}(\mathbf{\Lambda})$ approaches the noninteracting limit, which is given by the second term in Eq. (12). We determine the scalar susceptibility from the linear relation $\mathbf{Q} = \chi\mathbf{\Lambda}/N$, Eq. (C3), valid for small $\mathbf{\Lambda}$ in the isotropic regime. The result is shown in the inset of Fig. 1, together with a fit to $\chi(T) = -2/15 + b/(T^* - T_c^*)$, where $T^* = 1/(\beta J)$ is the dimensionless temperature. From these fits, we obtain a rough estimate for the critical temperature T_c^*. The susceptibility for a weak ordering field near the transition has already been evaluated numerically in Refs. [37,41]. The effect of interactions is described by the first term therein, where z^* is the only unknown parameter. Fitting the numerical values to $c_1 = 1/\chi = z^*\beta J - 15/2$, we obtain the effective coordination number z^*. For temperatures above the transition, we find $z^* \approx 3.4 \pm 0.1$ for the square lattice in two dimensions, somewhat lower than the mean-field value $z = 4$. A reduction of the mean-field value is expected due to fluctuation corrections which reduce the mean molecular field acting on each spin [19]. Similarly, we also find a value of $z^* \approx 5.6 \pm 0.1$ lower than 6 for the three-dimensional model on a cubic lattice. A constant value of z^* leads to a temperature-independent prefactor A_0 in Eq. (1) and therefore agrees with the classical Landau–de Gennes theory. Deviation from a constant, temperature-independent value appears near the transition. This finding is in line with Ref. [37], which observed disagreement in the orientational correlation function between the Lebwohl-Lasher model and Landau–de Gennes theory near the transition. We note that a method for calculating the effective coordination number is provided by the cluster variational approximation [42]. The values of the effective coordination numbers and estimates for the critical temperature for the different lattices investigated are summarized in Table I. Further studies are certainly needed in order to determine the critical temperature for the honeycomb, semitriangular, and hexagonal lattice more accurately. We refrain here from pursuing this further, since the aim of the present paper is an expression for the macroscopic free energy of these systems, for which the precise value of T_c^* is not crucial.

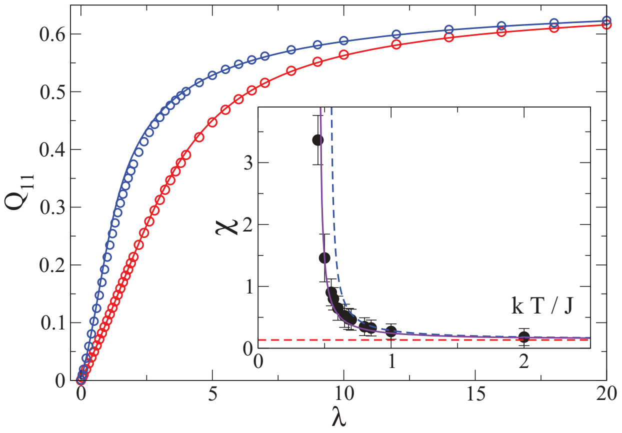

FIG. 1. (Color online) The order parameter Q_{11} of the Lebwohl-Lasher model on a square lattice as a function of the Lagrange multiplier λ for $\beta J = 1.0$ (top) and 0.125 (bottom). A uniaxial form of the Lagrange multiplier is chosen. Symbols denote the numerical values from Monte Carlo simulations, and the lines are obtained from fits to Eq. (12). Inset: The susceptibility $\chi = 1/c_1$ between $\mathbf{Q}$ and $\mathbf{\Lambda}$ [Eq. (C3)] as a function of temperature. The symbols denote the numerical values obtained from linear regression, for values $|\mathbf{\Lambda}/N| < 0.1$. The broken line is the mean-field prediction from Eq. (C7), and the full line is the fit mentioned in the text.

TABLE I. Coordination and effective coordination number z and z^*, respectively, as well as estimates for the critical temperature $T_c^* = k_BT_c/J$ for the different lattices investigated. Numbers in brackets are the uncertainty in the last digit.

Lattice	Honeycomb	Square	Semitriang.	Hexagonal	Cubic
z	3	4	5	6	6
z^*	2.1(1)	3.4(1)	4.2(1)	5.4(2)	5.6(1)
T_c^*	0.236(4)	0.375(5)	0.48(1)	0.653(6)	0.76(2)

D. Universal form of ideal entropy

From the numerical data of $\mathbf{Q}(\mathbf{\Lambda})$, we perform thermodynamic integration using Eq. (6) to arrive at the effective free energy $\mathcal{F}(\mathbf{Q})$. Due to frame invariance, the resulting effective free energy $\mathcal{F}$ can depend on tensorial invariants of $\mathbf{Q}$ only. In order to test the form of the macroscopic free energy (11), we subtract from $\mathcal{F}(\mathbf{Q})$ the effective mean-field interaction term, $\Delta f \equiv \mathcal{F}(\mathbf{Q})/Nk_BT + (1/2)z^*\beta J\mathrm{tr}\{\mathbf{Q}\cdot\mathbf{Q}\}$. In the uniaxially ordered state around the director $\mathbf{n}$, the order parameter tensor can be written as $\mathbf{Q} = S_2\overline{\boldsymbol{nn}}$, where the Maier-Saupe order parameter S_2 is defined as $S_2 = \langle P_2(\mathbf{u}\cdot\mathbf{n})\rangle_{\mathbf{\Lambda}}$. The director

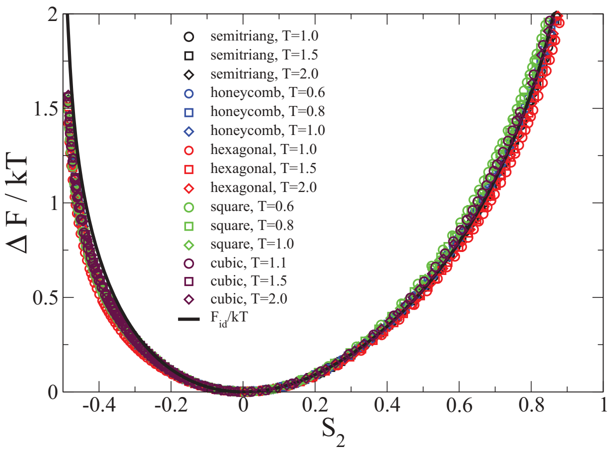

FIG. 2. (Color online) Dimensionless difference $\Delta f = \Delta F/k_{\rm B}T$ between the effective free energy (6) and the mean effective interaction energy defined in the text as a function of the Maier-Saupe order parameter S_2. Different symbols correspond to different lattice symmetries. The data nicely collapse onto a single master curve. The thick solid line represents the scaled ideal orientational entropy $-S^{\rm id}/Nk_{\rm B}$, which describes the numerically obtained master curve very well.

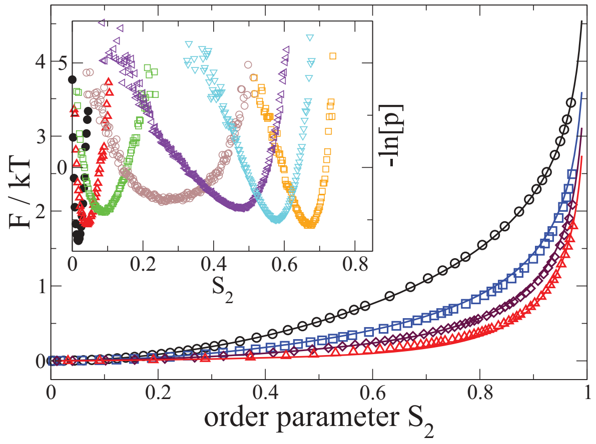

FIG. 3. (Color online) The dimensionless effective free energy $\mathcal{F}/Nk_{\rm B}T$ as a function of the Maier-Saupe order parameter S_2 for the planar Lebwohl-Lasher model on a square lattice. The reduced temperature $k_{\rm B}T/J$ is decreasing from top to bottom as 8.0, 1.0, 0.7, 0.566. Symbols denote the numerical values while the lines are obtained from Eq. (11). Inset: The quantity $-\ln p(\mathbf{Q})$ defined in the text is shown as a function of S_2 for reduced temperatures, from left to right, 8.0, 0.566, 0.45, 0.40, 0.38, 0.35, 0.30.

n is given by the eigenvector of **Q** that corresponds to the largest eigenvalue. In the uniaxial state, the tensorial invariants simplify to $I_2 = S_2^2/3, I_3 = 2S_2^3/9$, and $\mathcal{Q} = 1 + 2S_2^3 - 3S_2^2$.

Figure 2 shows Δf as a function of S_2 for different strengths of the ordering field. As predicted by Eq. (11), all the data for different lattices collapse onto a single master curve, which is given by the ideal entropy $\Delta f = -S^{\rm id}/Nk_{\rm B} = -\ln(\sqrt{\mathcal{Q}}) - (2/3)[\sqrt{\mathcal{Q}} - 1]$. This result nicely demonstrates the universality of the ideal entropic contribution to the free energy.

E. Enhanced Landau-de Gennes free energy

Now that the ideal part of the free energy has been verified, we include also the interaction part. In Fig. 3 we show the effective free energy as a function of the Maier-Saupe order parameter S_2. We find very good agreement between the numerical data from thermodynamic integration and the analytical formula (11). It should be noted that the weak ordering as well as the divergence for perfectly ordered states is captured correctly by our effective free energy (11). Below the transition, one would need to modify Eq. (6) as the reference state is no longer isotropic. Instead, we test predictions that the free energy (11) makes for the nematic state below. For comparison, the inset of Fig. 3 shows the effective potential when obtained from equilibrium fluctuations $\beta(L(\mathbf{Q}) - F) = -N\ln[p(\mathbf{Q})]$, where p is the probability $p(\mathbf{Q}) = \langle\delta(\mathbf{Q} - \mathbf{\Pi})\rangle$. This quantity has been studied in Ref. [38] close to the phase transition. Even taking into account that the thermodynamic free energy F is a function of temperature, L and $\mathcal{F}$ are certainly quite different. Since equilibrium fluctuations of S_2 are small except near the phase transition, the potential L is rather stiff and the state space is not fully explored. In the generalized canonical ensemble, instead, the Lagrange multipliers force the system into a manifold of partially ordered states. Thus, $\mathcal{F}$ can be defined for practically all values of S_2 in the isotropic state.

F. Isotropic-nematic transition

Next, we want to test the predictions that the effective free energy $\mathcal{F}(\mathbf{Q})$ makes against simulations of the original Lebwohl-Lasher model. The most direct prediction of $\mathcal{F}$ is the isotropic-nematic phase transition.

Although the temperature dependence of the first term in Eq. (1) near the transition is more complicated than in the Landau–de Gennes theory, the isotropic-nematic phase transition can be discussed very much in the same way. The orientationally ordered phase is characterized by a nontrivial solution $\mathbf{Q} \neq 0$ for the equilibrium state $\partial\mathcal{F}/\partial\mathbf{Q} = 0$. Contracting Eq. (12) with $\mathbf{Q}$, one arrives at the implicit equation

$$z^*\beta J = 9\left(\frac{1}{2\mathcal{Q}} + \frac{1}{3\sqrt{\mathcal{Q}}}\right)(1 - S_2). \tag{13}$$

The solution of Eq. (13) is shown in Fig. 4, where the isotropic-nematic transition occurs through a saddle-node bifurcation. For the order parameter at the transition, we find $S_2(T_c) \approx 0.3433$, independent of dimension and symmetry of the lattice. This value is close to the theoretical result $S_2(T_c) = 0.32$ obtained from effective action in the hopping expansion (see Ref. [19] and references therein). It is interesting to note that these values are close to the experimental one $S_c = 0.312$ for MBBA [6]. Figure 4 also shows the results of our Monte Carlo simulations. Within numerical precision, the data indeed collapse onto a single master curve as predicted by Eq. (13). The functional form given in Eq. (13) provides a good description of the data. Upon closer inspection, however, the theoretical result seems to be slightly but systematically overpredicting the order parameters for the two-dimensional

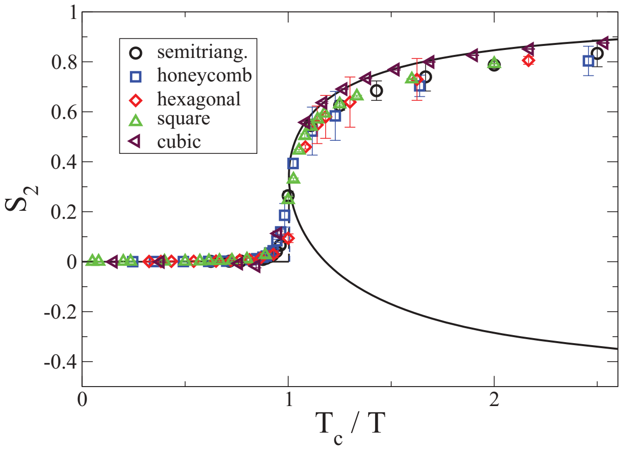

FIG. 4. (Color online) Bifurcation diagram shows the Maier-Saupe order parameter S_2 as a function of T_c/T. Solid lines are the solution of Eq. (13). Symbols denote the results of Monte Carlo simulations for different lattice symmetries.

systems. Better agreement might be obtained by a more careful consideration of the temperature dependence of z^*.

Monte Carlo simulations of the three-dimensional Lebwohl-Lasher model on a cubic lattice close to the transition have been performed in Ref. [37]. In these simulations, the orientational order parameter $S_2 = \langle P_2(\mathbf{u}\cdot\mathbf{n})\rangle$ has been evaluated as an ensemble average over instantaneous preferred directions. Alternatively, we determine S_2 here from our Monte Carlo simulations in the generalized canonical ensemble (2) via the linear-response formula (A3) in the limit of vanishing $\mathbf{\Lambda}$. In full analogy to the method of an infinitesimal biasing field in ferromagnets [23], spontaneous symmetry breaking due to the phase transition is replaced by a weak ordering field that breaks the symmetry in a controlled way. Figure 5 shows that the theoretical description is very accurate and performs better than the popular result $S_2^{\mathrm{D}} = \frac{1}{4} + \frac{3}{4}[1 - T/T_c]^{1/2}$ given in Ref. [13]. The critical exponent of $S_2(T) \sim (T_c - T)^{\beta}$ is $\beta = 1/2$, not only for S_2^{D} but also for result derived here, since both are mean-field theories. The exponent $\beta = 1/2$ does not seem to agree well with experimental observations [1]. It should be noted, however, that S_2^{D} predicts the scaling relation all the way to $T = 0$, while the scaling relation holds in our result only near the transition and crosses over to a weaker temperature dependence at lower temperatures.

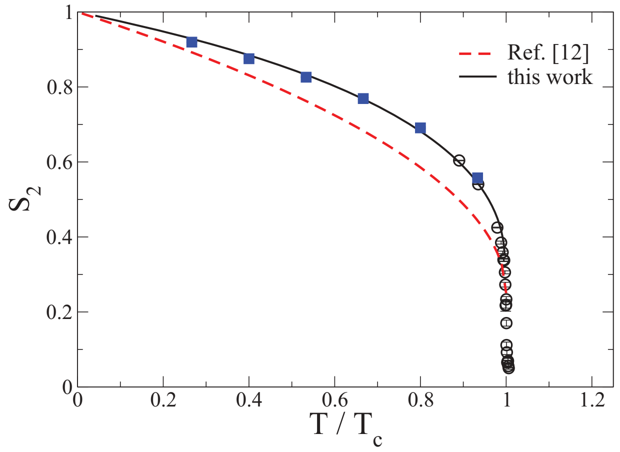

FIG. 5. (Color online) The Maier-Saupe orientational order parameter S_2 as a function of the scaled temperature T/T_c for the three-dimensional Lebwohl-Lasher model. Circles are the result of extensive, but standard Monte Carlo simulations [37], and squares denote the result of our Monte Carlo simulations in the generalized canonical ensemble (2), extrapolated for $\mathbf{\Lambda} \to 0$. The solid line is the theoretical prediction from the solution to Eq. (13), and the broken line is S_2^{D} from Ref. [13] defined in the text.

G. Ordering in an external field

As a further application of the effective free energy, we briefly discuss the induced orientational ordering due to external fields. In particular, we consider magnetic fields [2] and potential flows [3]. In both cases the stationary distribution is of the form (2) with $\mathbf{K} = -\frac{3}{4}\Delta\chi\overline{\mathbf{HH}}$ and $\mathbf{K} = -\frac{1}{2}\tau\mathbf{D}$ playing the role of $\mathbf{\Lambda}$ for magnetic and flow fields, respectively. Therefore, the effective free energy (11) also needs to be extended by a term $-N\mathbf{Q} : \mathbf{K}$. We denote the magnetic field by $\mathbf{H}$ and $\Delta\chi$ the anisotropy in the magnetic susceptibility. For potential (e.g., elongational) flows, the velocity gradient tensor $\mathbf{D}$ is symmetric. Finally, we have introduced the rotational relaxation time τ, which is related to the rotational diffusion of the rodlike particles [12].

The stationary state in the presence of external fields obeys $\beta\frac{\partial\mathcal{F}}{\partial\mathbf{Q}} - N\mathbf{K} = 0$. This condition is identical to Eq. (12) with $\mathbf{\Lambda}$ replaced by $N\mathbf{K}$. For illustration purposes, we choose uniaxial elongational flow with elongation rate $\dot{\epsilon}$, $\mathbf{D} = \dot{\epsilon}\overline{\boldsymbol{nn}}$. Note that the tensorial form of $\mathbf{K}$ is identical in the case of an applied magnetic field. The condition of stationarity (D2) with $k = \frac{1}{2}\tau\dot{\epsilon}$ provides the implicit equation $\dot{\epsilon}(S_2)$ from which we obtain $S_2(\dot{\epsilon})$ numerically. Figure 6 shows the Maier-Saupe order parameter S_2 as a function of the dimensionless applied elongational rate $\tau\dot{\epsilon}$ (Weissenberg number). We observe that

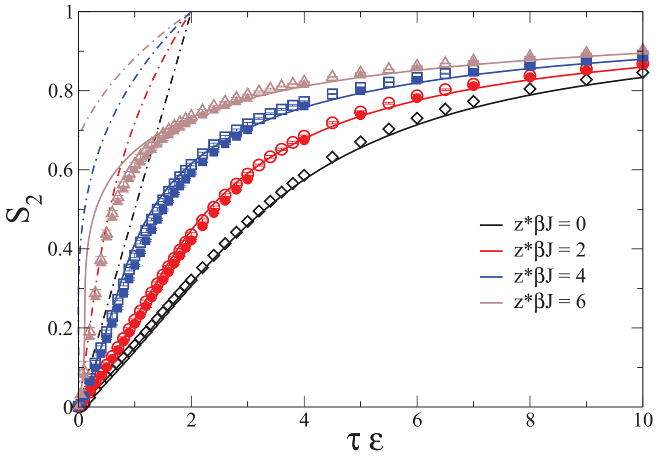

FIG. 6. (Color online) The Maier-Saupe orientational order parameter S_2 as a function of the dimensionless elongation rate $\tau\dot{\epsilon}$. From bottom to top, the interaction strength is increasing as $z^*\beta J = 0,2,4,6$. Solid lines show the prediction of Eq. (D2), and broken lines correspond to the Doi-Edwards form (D4). Open and full symbols denote the result of Monte Carlo simulations of the two- and three-dimensional Lebwohl-Lasher model, respectively.

$S_2(\dot{\epsilon})$ is a monotonically increasing function, linear for small $\tau\dot{\epsilon}$ and approaching the maximum value $S_2 = 1$ for infinitely strong flow. We find that the theoretical prediction (D2) is in very good agreement with Monte Carlo simulations, except for weak flows close to the phase transition. The range of validity of the fourth-order expansion (D3) shrinks from $\tau\dot{\epsilon} \lesssim 3$ for $z^*\beta J = 0$ down to $\tau\dot{\epsilon} \lesssim 0.1$ for $z^*\beta J = 6$.

IV. CONCLUSIONS

We here present a systematic approach for calculating the effective free energy for nematics starting from a microscopic model system. The method we propose and test uses thermodynamic integration within the generalized canonical ensemble and therefore fits well into recent coarse-graining approaches.

We test the proposed method for the two- and three-dimensional Lebwohl-Lasher model. With Eq. (11), we find a new form of the effective free energy $\mathcal{F}$ for nematics. Compared to the standard Landau–de Gennes expansion (1), the new expression has several advantages: (1) It is well founded microscopically, so that the coefficients and their temperature-dependence can be calculated for a given model system. (2) Energetic and entropic effects are clearly separated, and their interpretation is evident. (3) The entropic penalty for orientational ordering leads to a logarithmically diverging barrier that prevents unphysical values of the order parameter. Therefore, $\mathcal{F}$ is not limited to the near-transition region. (4) Finally, for weak orientational ordering, the Landau–de Gennes expansion is recovered.

The explicit expression for the effective free energy that we derive here can directly be used to replace the usual fourth-order expansion. On the macroscopic level, the relaxational dynamics reads [12,13],

$$\frac{d}{dt}\mathbf{Q} = -\frac{1}{N\tau k_B T}\frac{\partial \mathcal{F}}{\partial \mathbf{Q}} = \frac{1}{N\tau}\mathbf{\Lambda}, \tag{14}$$

where the Lagrange multiplier $\mathbf{\Lambda}$ for the Lebwohl-Lasher model is given by Eq. (12) with $\mathcal{Q}$ defined after Eq. (11). The description of transient dynamics of nematics in a flow field is beyond the scope of this manuscript. The clear separation of $\mathcal{F}$ into energetic and entropic contributions, however, facilitates the formulation of the corresponding time evolution equations for $\mathbf{Q}$ within the GENERIC framework of nonequilibrium thermodynamics [29].

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APPENDIX A: CUMULANT EXPANSION

From Eq. (3), the generating function $G(\mathbf{\Lambda})$ can be expressed as a cumulant expansion

$$\begin{aligned} G(\mathbf{\Lambda}) &= G(0) - k_B T \ln\langle e^{-\mathbf{\Lambda}:\mathbf{\Pi}}\rangle \\ &= G(0) - k_B T \sum_{n=1}^{\infty} \frac{(-1)^n}{n!}\langle(\mathbf{\Lambda}:\mathbf{\Pi})^n\rangle^c, \end{aligned} \tag{A1}$$

where $\langle\bullet\rangle$ denotes equilibrium averages with $\mathbf{\Lambda} = 0$ and $\langle\bullet\rangle^c$ are cumulants. Inserting the cumulant expansion into in Eq. (4), the order parameter is given by

$$\mathbf{Q}(\mathbf{\Lambda}) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!}\langle(\mathbf{\Lambda}:\mathbf{\Pi})^n\mathbf{\Pi}\rangle^c. \tag{A2}$$

Unfortunately, this equation cannot be inverted in general to give an explicit relation for $\mathbf{\Lambda}(\mathbf{Q})$.

Expanding G to second order in $\mathbf{\Lambda}$, we obtain

$$\mathbf{Q} = \mathbf{Q}_0 - \mathbf{C}_0 : \mathbf{\Lambda}/N + O(\mathbf{\Lambda}^2), \tag{A3}$$

where $\mathbf{Q}_0 = \langle\mathbf{\Pi}\rangle$ is the equilibrium order parameter for $\mathbf{\Lambda} = 0$ and $\mathbf{C}_0 = \langle\mathbf{\Pi}\mathbf{\Pi}\rangle^c$ the equilibrium fluctuations of the order parameter. Solving for $\mathbf{\Lambda}$ and inserting the result into Eq. (5), we obtain the effective free energy as a quadratic form:

$$\mathcal{F}(\mathbf{Q}) = F + \tfrac{1}{2}Nk_B T(\mathbf{Q}-\mathbf{Q}_0) : \mathbf{C}_0^{-1} : (\mathbf{Q}-\mathbf{Q}_0) + \cdots. \tag{A4}$$

Such an effective free energy forms the basis of Einstein's fluctuation theory [29]. In the fully isotropic state $\mathbf{Q}_0 = 0$, $\mathbf{Q} = -(2/15)\mathbf{\Lambda}$ and $\mathcal{F} = F + (15/4)Nk_B T \,\mathrm{tr}\{\mathbf{Q}^2\}$.

APPENDIX B: SADDLE-POINT APPROXIMATION

Start with the Hamiltonian of the Lebwohl-Lasher model (7),

$$H' = -\frac{1}{2}\sum_{ij} J_{ij}\overline{\mathbf{u}_i\mathbf{u}_i} : \overline{\mathbf{u}_j\mathbf{u}_j} + \frac{1}{N\beta}\mathbf{\Lambda} : \sum_j \overline{\mathbf{u}_j\mathbf{u}_j}, \tag{B1}$$

where $J_{ij} = J$ if i and j are nearest neighbors and zero otherwise. As usual, we invoke the Hubbard-Stratonovich transformation [23],

$$1 = (\det\beta J)^{1/2}\int \mathcal{D}\boldsymbol{\phi}\, e^{-\beta/2\sum_{ij} J_{ij}(\boldsymbol{\phi}_i - \overline{\mathbf{u}_i\mathbf{u}_i}):(\boldsymbol{\phi}_j - \overline{\mathbf{u}_j\mathbf{u}_j})}, \tag{B2}$$

with $\int\mathcal{D}\boldsymbol{\phi} = \prod_{k=1}^{N}\int_{-\infty}^{\infty}\frac{d\boldsymbol{\phi}_k}{\sqrt{2\pi}}$, in order to rewrite the generating function (3) as

$$e^{-\beta G(\mathbf{\Lambda})} = \int \mathcal{D}\boldsymbol{\phi}\, e^{-S_{\mathbf{\Lambda}}[\boldsymbol{\phi}]} \tag{B3}$$

with the effective action

$$\begin{aligned} S_{\mathbf{\Lambda}}[\boldsymbol{\phi}] = &-\frac{1}{2}\ln\det(\beta J) + \frac{\beta}{2}\sum_{ij} J_{ij}\boldsymbol{\phi}_i : \boldsymbol{\phi}_j \\ &- \sum_j G_{\mathrm{id}}\Big(\beta\sum_i J_{ij}\boldsymbol{\phi}_i - \mathbf{\Lambda}/N\Big), \end{aligned} \tag{B4}$$

where $G_{\mathrm{id}}(\mathbf{A})$ is the generating function for the ideal, noninteracting system [33].

Equations (B3) and (B4) can be used as starting point for perturbation theories [19]. The saddle-point approximation is given by

$$\left.\frac{\partial S_{\mathbf{\Lambda}}[\boldsymbol{\phi}]}{\partial\boldsymbol{\phi}_i}\right|_{\bar{\boldsymbol{\phi}}} = 0 = \beta\sum_j J_{ij}\bar{\boldsymbol{\phi}} - z\beta J\left.\frac{\partial G_{\mathrm{id}}(\mathbf{A})}{\partial\mathbf{A}}\right|_{z\beta J\mathbf{Q}-\mathbf{\Lambda}}, \tag{B5}$$

from which $\bar{\boldsymbol{\phi}} = \mathbf{Q}$ follows. In this approximation, the generating function is given by

$$G(\mathbf{\Lambda}) \approx S_{\mathbf{\Lambda}}[\bar{\boldsymbol{\phi}}] = S_0 - NG_{\mathrm{id}}(z\beta J\mathbf{Q} - \mathbf{\Lambda}/N), \tag{B6}$$

where S_0 is independent of $\mathbf{\Lambda}$ and therefore irrelevant in G. Nevertheless, it is interesting to observe the occurrence of the mean-field interaction energy term $\frac{1}{2}Nz\beta J\mathbf{Q}:\mathbf{Q}$ that appears in S_0 upon inserting $\bar{\boldsymbol{\phi}} = \mathbf{Q}$ in (B4).

APPENDIX C: MEAN-FIELD FREE ENERGY OF THE LEBWOHL-LASHER MODEL

In mean-field approximation, the generating function (3) for the Lebwohl-Lasher model is given by

$$\begin{aligned} G_{\mathrm{LL}}^{\mathrm{MFA}}(N,T,\mathbf{\Lambda}) &= -Nk_{\mathrm{B}}T \ln \int d\mathbf{u} \exp\left[(z\beta J\mathbf{Q} - \mathbf{\Lambda}/N) : \overline{\mathbf{uu}}\right] \\ &= -NG_{\mathrm{id}}(z\beta J\mathbf{Q} - \mathbf{\Lambda}/N) - Nk_{\mathrm{B}}T \ln(4\pi), \end{aligned} \tag{C1}$$

where $G_{\mathrm{id}}(\mathbf{A}) = {}_1F_1(1/2,3/2,\mathbf{A})$ is the generating function of the ideal, noninteracting system and ${}_1F_1$ the confluent hypergeometric function of matrix argument [33]. From $\mathbf{Q} = (Nk_{\mathrm{B}}T)^{-1}\partial G_{\mathrm{LL}}^{\mathrm{MFA}}/\partial\mathbf{\Lambda}$ find [33],

$$\mathbf{Q} = \frac{2}{15}\mathbf{A} + \frac{4}{105}\overline{\mathbf{A}.\mathbf{A}} - \frac{4}{1575}\mathrm{tr}\{\mathbf{A}^2\}\mathbf{A} + O(\mathbf{A}^4) \tag{C2}$$

with $\mathbf{A} = z\beta J\mathbf{Q} - \mathbf{\Lambda}/N$. Use the following ansatz for the unknown function $\mathbf{\Lambda}(\mathbf{A})$,

$$\mathbf{\Lambda}/N = c_1\mathbf{Q} + c_2\overline{\mathbf{Q}.\mathbf{Q}} + c_3\overline{\mathbf{Q}.\mathbf{Q}.\mathbf{Q}} + c_3'\mathrm{tr}\{\mathbf{Q}^2\}\mathbf{Q} + O(\mathbf{Q}^4) \tag{C3}$$

with some coefficients c_k. This leads to

$$\mathbf{A} = \bar{c}_1\mathbf{Q} - c_2\overline{\mathbf{Q}.\mathbf{Q}} - c_3\overline{\mathbf{Q}.\mathbf{Q}.\mathbf{Q}} - c_3'\mathrm{tr}\{\mathbf{Q}^2\}\mathbf{Q} + O(\mathbf{Q}^4) \tag{C4}$$

with $\bar{c}_1 = z\beta J - c_1$ and

$$\begin{aligned} \mathbf{A}\cdot\mathbf{A} = \bar{c}_1^2\mathbf{Q}\cdot\mathbf{Q} - 2\bar{c}_1c_2\mathbf{Q}\cdot\mathbf{Q}\cdot\mathbf{Q} \\ + \tfrac{2}{3}\bar{c}_1c_2\mathrm{tr}\{\mathbf{Q}^2\}\mathbf{Q} + O(\mathbf{Q}^4). \end{aligned} \tag{C5}$$

Inserting these expressions into Eq. (C2), find

$$\begin{aligned} 0 = \left(\frac{2}{15}\bar{c}_1 - 1\right)\mathbf{Q} + \left(-\frac{2}{15}c_2 + \frac{4}{105}\bar{c}_1^2\right)\mathbf{Q}\cdot\mathbf{Q} \\ + \left(-\frac{2}{15}c_3' + \frac{8}{315}\bar{c}_1c_2 - \frac{4}{1575}\bar{c}_1^3\right)\mathrm{tr}\{\mathbf{Q}^2\}\mathbf{Q} \\ + \left(-\frac{2}{15}c_3 - \frac{8}{105}\bar{c}_1c_2\right)\overline{\mathbf{Q}.\mathbf{Q}.\mathbf{Q}} + O(\mathbf{Q}^4). \end{aligned} \tag{C6}$$

Requiring this equality to hold to all orders in $\mathbf{Q}$, we find that the coefficients are given by

$$c_1 = z\beta J - \frac{15}{2}, \quad c_2 = \frac{225}{14}, \quad c_3 = -\frac{3375}{49}, \quad c_3' = \frac{2925}{196}. \tag{C7}$$

APPENDIX D: FIELD-INDUCED ORIENTATION

An external field leads to an additional energetic contribution to the effective free energy, $\mathcal{F} \to \mathcal{F}' = \mathcal{F} + N\beta^{-1}\mathbf{K}:\mathbf{Q}$. Stable stationary states correspond to minima of $\mathcal{F}'$,

$$\mathbf{K} = z^*\beta J\mathbf{Q} + 9s'[3\overline{\mathbf{Q}.\mathbf{Q}} - \mathbf{Q}], \tag{D1}$$

where $s' = (2\mathcal{Q})^{-1} + (9\mathcal{Q})^{-1/2}$. For the special case of uniaxial symmetry $\mathbf{K} = k\overline{\boldsymbol{nn}}$, $\mathbf{Q} = S_2\overline{\boldsymbol{nn}}$, Eq. (D1) simplifies to

$$-k = z\beta J S_2 + 9s'S_2(S_2 - 1), \tag{D2}$$

with $\mathcal{Q} = 1 + 2S_2^3 - 3S_2^2$. Equation (D2) determines the function $S_2(k)$ implicitly. For weak ordering, we can solve the equation perturbatively via the ansatz $S_2 = \sum_n \alpha_n k^n$ and requiring Eq. (D2) to hold to all orders in k. Up to fourth order, the expansion reads

$$\begin{aligned} S_2 = -\chi k - \frac{15}{2}\chi^3k^2 - 18\left(z^*\beta J - \frac{5}{4}\right)\chi^5k^3 \\ -30\left([z^*\beta J]^2 + \frac{15}{2}z^*\beta J - \frac{675}{16}\right)\chi^7k^4 + O(k^5), \end{aligned} \tag{D3}$$

where $\chi = c_1^{-1}$ and the coefficient c_1 has already been defined in Eq. (C7).

For comparison, we remind the reader that the stationary state for the Doi-Edwards free energy $\mathcal{F}^{\mathrm{D}}$ is determined from the cubic equation

$$k = \left(1 - \frac{U}{3}\right)S_2 - \frac{1}{3}US_2^2 + \frac{2}{3}US_2^3. \tag{D4}$$

It is apparent from this expression that S_2 grows unbounded as the strength of the ordering field increases. This artifact can be traced back to the simple quadratic form of the free energy for the noninteracting case. Note that increasing the interaction strength U does not prevent the solution to exceed the maximum value $S_2 = 1$, as all curves coincide at $k = 2$, irrespective of the value of U.

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