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Ideal contribution to the macroscopic quasiequilibrium entropy of anisotropic fluids

Patrick Ilg,¹ Markus Hütter,² and Martin Kröger¹

¹*ETH Zürich, Department of Materials, Polymer Physics, HCI H541, CH-8093 Zürich, Switzerland*
²*Eindhoven University of Technology, Mechanical Engineering, Materials Technology, PO Box 513, WH 4.136, 5600 MB Eindhoven, The Netherlands*

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The Landau-de Gennes free energy plays a central role in the macroscopic theory of anisotropic fluids. Here, the ideal, entropic contribution to this free energy—that is always present in these systems, irrespectively of the detailed form of interactions or applied fields—is derived within the quasiequilibrium ensemble and successfully tested. An explicit and compact form of the macroscopic, ideal entropy is derived. This entropy is nonpolynomial in the order parameter, diverging logarithmically near the fully oriented state and therefore restricting the order parameter to physical admissible values. As an application, it is shown that the isotropic-nematic transition within the Maier-Saupe model is described in a simple and very accurate manner.

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I. INTRODUCTION

Anisotropic liquids are often modeled on the level of kinetic theory, where their state is described by the single-particle orientational distribution function. Examples comprise liquid crystals and liquid-crystalline polymers [1], general colloidal suspensions of anisotropic (e.g., fiber suspensions) or dipolar (e.g., ferrofluids) particles [2], and more recently also suspensions of self-propelled particles [3]. The Fokker-Planck or Smoluchowski equation provides a solid physical framework, which is flexible enough to include different types of (typically mean-field) interactions as well as dynamical and flow properties [4–7].

For many purposes, however, a more macroscopic description is sufficient, where the systems are described by the orientational order parameter [8]. Such a macroscopic description is of course more economical and therefore often preferred for large-scale numerical simulations. The formulation of the model in terms of order parameters has the additional benefit of concentrating on the essential physical mechanisms [9]. For the macroscopic theory of anisotropic fluids, the Landau-de Gennes free energy is the important cornerstone [1]. However, different variants of the macroscopic theory have been proposed that should correspond to the same underlying system. Many different closure approximations have been suggested in the past, in order to arrive at closed-form macroscopic equations (see, e.g., Refs. [10,11] and references therein). Identifying an effective Landau-de Gennes free energy *a posteriori* [5,12], it is often overlooked that these closure approximations also change static properties, like the location of the isotropic-nematic transition in liquid-crystals. One should also mention that the classical, fourth-order Landau-de Gennes potential was meant to describe the vicinity of the phase transition and is therefore not reliable when used naively in strong external (electric or magnetic) fields or flows. This deficiency has been noted several times in the literature [13–16] and, e.g., led to the suggestion of an empirical penalty function [13]. An extended effective free energy for liquid-crystals based on Onsager’s excluded volume entropy functional [17] is explored, e.g., in Refs. [18,19]. Here, we focus on the ideal, entropic contribution to the effective free energy of noninteracting orientational degrees of

freedom, which is present in all anisotropic fluids, in addition to specific interaction or field-contributions. It is shown that this ideal entropy is quadratic in the order parameter only near the isotropic state but nonpolynomial in general. We derive the macroscopic form of the ideal entropy within the quasiequilibrium ensemble that is obtained from the maximum entropy principle. For weak uniaxial ordering, our results reduce to those obtained in Ref. [15]. For strong ordering, on the other hand, the entropy diverges logarithmically near the fully oriented state, thereby limiting the order parameter to physically admissible values.

II. ORIENTATIONAL ENTROPY

In this work, only spatially homogeneous systems are considered in order to concentrate exclusively on the ideal orientational entropy. For also including translational degrees of freedom and spatial inhomogeneities, see, e.g., Refs. [8,20,21] and references therein.

A. Boltzmann entropy

Let $f(\mathbf{u})$ denote the orientational distribution function, with $\mathbf{u} \in \mathcal{S}^2$ a three-dimensional vector on the unit sphere \mathcal{S}^2 . For a proper probability density, f has to be positive semidefinite $f \geq 0$ and normalized, $\int d^2u f(\mathbf{u}) = 1$, where the integration is performed over \mathcal{S}^2 . The Boltzmann entropy functional for ideal (noninteracting) anisotropic fluids is given by

$$S_0[f] = S_{\text{iso}} - k_B \int d^2u f(\mathbf{u}) \ln[4\pi f(\mathbf{u})], \quad (1)$$

with k_B the Boltzmann constant. In the isotropic state, $f(\mathbf{u}) = 1/(4\pi)$, $S_0[f]$ reaches its maximum value S_{iso} . Therefore, the equilibrium state is isotropic in the absence of interactions or external fields. For simplicity, we set $S_{\text{iso}} = 0$ in the following.

The total free energy can be written as

$$F(f) = -T[S_0(f) + S_{\text{ex}}(f)] + E(f), \quad (2)$$

where S_{ex} denotes the excess entropy due to entropic (excluded volume) interactions [17,18]. Energetic interactions and external field effects are included in the energy functional E .

B. Orientational order parameters

Deviations from the isotropic state can be quantified via the scalar orientational order parameter, defined by

$$S_2 = \int d^2u P_2(\mathbf{u} \cdot \mathbf{n}) f(\mathbf{u}), \quad (3)$$

where $P_2(x)$ is the second Legendre polynomial, $P_2(x) = (3x^2 - 1)/2$, and \mathbf{n} denotes the axis of mean orientation, the so-called ‘‘director’’ [1]. The isotropic state is characterized by $S_2 = 0$, while $S_2 = 1$ and $-1/2$ correspond to the perfectly parallel and planar alignment, respectively. Note that S_2 is invariant under inversion $\mathbf{n} \rightarrow -\mathbf{n}$, as required by the head-tail symmetry $\mathbf{u} = -\mathbf{u}$ of anisotropic particles. An exception are polar fluids, where the average orientation is nonvanishing and proportional to the average polarization.

Equation (3) characterizes the orientational ordering in the case of uniaxial symmetry around the director \mathbf{n} . In the general case, the orientational ordering can show biaxial symmetry [2] and the order parameter is represented by a symmetric second rank, so called alignment or order parameter tensor

$$\mathbf{Q} = \int d^2u [\mathbf{u}\mathbf{u} - (1/3)\mathbf{1}] f(\mathbf{u}), \quad (4)$$

where $\mathbf{1}$ is the three-dimensional unit matrix. From Eq. (4), the scalar order parameter (3) can be obtained from \mathbf{Q} by $S_2 = \frac{3}{2} \mathbf{nn} : \mathbf{Q}$.

C. Canonical distribution functions

On a macroscopic level, anisotropic fluids can be described solely in terms of orientational order parameters, without reference to underlying probability densities. A cornerstone of this macroscopic description is an effective Landau-de Gennes free-energy $F^*(S_2)$ for the order parameter [1]. Different routes to such a macroscopic description have been proposed in the past, resulting in different, nonequivalent formulations. Powerful thermodynamic approaches have been developed [8] that allow formulation of the macroscopic model directly. Unfortunately, however, this approach does not allow derivation of the different terms and coefficients and, therefore, it is possible neither to identify the microscopic origin of the coefficients in the Landau-de Gennes free energy nor to derive higher-order corrections.

Here, we suggest a statistical mechanics derivation of the ideal contribution to the macroscopic entropy $S_0^*(S_2)$. Due to the elimination of degrees of freedom, the derivation shares the common problem of statistical physics that it is not unique and depends on chosen approximations. Typically, the Landau-de Gennes free energy is identified *a posteriori*, after using closure approximations that have been suggested for predicting dynamical properties [12]. Since the entropy S_0 is a static quantity, there is in principle no need to rely on such closures.

What is needed, however, is the choice of a relevant ensemble corresponding to the macroscopic level. Onsager suggested in Ref. [17] a one-parametric family of distribution functions (A1) mainly for analytical convenience, see Appendix A. Nevertheless, the highly nonlinear behavior of the entropy as a function of this parameter gives little hope of obtaining a simple form of the macroscopic entropy.

For the subsequent derivation, we now turn to a more realistic ensemble. In many cases, ranging from polymer solutions and melts, liquid-crystalline systems, polar liquids, the quasiequilibrium ensemble derived from the maximum entropy principle provides a good description of the chosen macroscopic quantities of interest [22]. In the context of liquid-crystalline systems, the corresponding ensemble is represented by the family of Bingham distributions [23,24],

$$\bar{f}(\mathbf{u}) = \frac{1}{4\pi} \exp[\mathbf{u} \cdot \mathbf{A} \cdot \mathbf{u} - G(\mathbf{A})]. \quad (5)$$

Without loss of generality, the symmetric matrix \mathbf{A} is chosen as trace-free from now on. Positivity of the distributions [Eq. (5)] is obvious. The normalization is ensured by the cumulant generating function

$$G(\mathbf{A}) = \ln \frac{1}{4\pi} \int d^2u e^{\mathbf{u} \cdot \mathbf{A} \cdot \mathbf{u}} = {}_1F_1\left(\frac{1}{2}, \frac{3}{2}, \mathbf{A}\right), \quad (6)$$

where ${}_1F_1(a, b, \mathbf{A})$ is the confluent hypergeometric function of matrix argument [23]. The function $G(\mathbf{A})$ has the properties $G(\mathbf{0}) = 0$ and $\mathbf{Q} = \partial G / \partial \mathbf{A}$. Higher order cumulants are derived by higher derivatives of $G(\mathbf{A})$. Thereby, the constraint $\text{tr}(\mathbf{A}) = 0$ should be imposed only after the derivative of the generating function has been taken in order to ensure the resulting \mathbf{Q} is indeed traceless. The ensemble of Eq. (5) is found to provide reliable predictions under various circumstances, even nonequilibrium flow situations [10,25,26]. Moreover, Eq. (5) describes the canonical equilibrium distribution in the presence of an applied field (when the particles have no permanent dipole moment) or a mean-field-type interaction, as well as the stationary distribution in uniaxial elongational flow for a suitable choice of the tensor \mathbf{A} proportional to the elongation rate [27].

III. MACROSCOPIC ENTROPY

With the relevant ensemble \bar{f} , Eq. (5), the macroscopic entropy is defined by $S^*(\mathbf{Q}) \equiv S_0[\bar{f}]$, i.e., the microscopic expression evaluated with the relevant distributions [15,22,28]. Inserting Eq. (5) into (1), the macroscopic entropy can be written as

$$S_0^*(\mathbf{Q})/k_B = -\mathbf{Q} : \mathbf{A} + G. \quad (7)$$

Therefore, S_0^* is the Legendre transform of G , which expresses the thermodynamically consistent change of independent variables from \mathbf{A} to \mathbf{Q} . An explicit form of $S_0^*(\mathbf{Q})$ is difficult to achieve, since the relation $\mathbf{A}(\mathbf{Q})$ needed to eliminate \mathbf{A} from Eq. (7) is known only implicitly.

For weak orientational ordering, the first terms in the expansion of $G(\mathbf{A})$ are given by Eq. (B4). From this, a series expansion of \mathbf{A} in \mathbf{Q} can be obtained; see Eq. (B6). Inserting these expressions into Eq. (7), the macroscopic entropy has the following expansion valid for weak orientational ordering:

$$S_0^*(\mathbf{Q})/k_B = -\frac{15}{4} \text{tr}(\mathbf{Q} \cdot \mathbf{Q}) + \frac{75}{14} \text{tr}(\mathbf{Q} \cdot \mathbf{Q} \cdot \mathbf{Q}) - \frac{3825}{784} [\text{tr}(\mathbf{Q} \cdot \mathbf{Q})]^2 + \mathcal{O}(\mathbf{Q}^5). \quad (8)$$

In Eq. (8), we made use of the fact that $\text{tr}(\mathbf{Q} \cdot \mathbf{Q} \cdot \mathbf{Q} \cdot \mathbf{Q}) = (1/2)[\text{tr}(\mathbf{Q} \cdot \mathbf{Q})]^2$, see, e.g., Eq. (10.59) in Ref. [29]. Equation (8) differs from the corresponding expression, Eqs. (10.41) and (10.50) given in Ref. [12], $S_0^{\text{DE}}(\mathbf{Q})/k_B = -(1/2)\text{tr}(\mathbf{Q} \cdot \mathbf{Q})$. It is worth mentioning that S_0^{DE} does not only fail for strongly ordered states, but is also in contradiction with Einstein's fluctuation theory [30]. In the present context, the latter states that the fluctuations in the isotropic state $\langle \mathbf{Q}\mathbf{Q} \rangle_{\text{iso}} = (4\pi)^{-1} \int d^2u \mathbf{Q}\mathbf{Q} = (15/2)\mathbf{1}$ are identical to $\langle \mathbf{Q}\mathbf{Q} \rangle_{\text{iso}} = -k_B^{-1}(\partial^2 S_0^*/\partial \mathbf{Q}\partial \mathbf{Q})_{\mathbf{Q}=0}$, which is indeed fulfilled for Eq. (8).

For the important special case of uniaxial symmetry around the director \mathbf{n} , the alignment tensor \mathbf{Q} can be written as $\mathbf{Q} = S_2(\mathbf{nn} - \frac{1}{3}\mathbf{1})$, where the (Maier-Saupe) order parameter S_2 has been defined in Eq. (3). The expression for the entropy [Eq. (7)] reads in case of uniaxial symmetry

$$S_0^*(S_2)/k_B = -\frac{2}{3}a(S_2)S_2 + G_{\text{uni}}[a(S_2)], \quad (9)$$

where G_{uni} is the corresponding generating function defined in Eq. (B7). G_{uni} can be evaluated in terms of the complementary error function, Eq. (B8), from which the following asymptotic expressions can be derived:

$$S_0^*(S_2)/k_B = \begin{cases} -\frac{5}{2}S_2^2 + \frac{25}{21}S_2^3 - \frac{425}{196}S_2^4, & |S_2| \ll 1 \\ \ln(1 - S_2) + 1 - \ln 3, & S_2 \rightarrow 1 \\ \frac{1}{2} \ln\left(\frac{1}{2} + S_2\right) + c_{1/2}, & S_2 \rightarrow -\frac{1}{2}, \end{cases} \quad (10)$$

with $c_{1/2} = \frac{1}{2}[1 + \ln(\frac{4\pi}{3})] - \ln(2)$. The fourth-order expansion in Eq. (10) for weak ordering has been previously derived, see Eq. (4.22) of Ref. [15]. The asymptotic behavior of the entropy near the perfectly aligned ($S_2 = 1$) and perfect planar-ordered ($S_2 = -1/2$) state are less known. A simple and rather accurate interpolation formula between these limiting cases is provided by

$$S_0^*(S_2)/k_B = \ln[(1 - S_2)(1 + 2S_2)^{1/2}] - S_2^2 + \frac{4}{21}S_2^3 + S_2^4 \left[\frac{38}{21} - \frac{3}{2} \ln(3) \right]. \quad (11)$$

Figure 1 shows the dimensionless entropy $S_0^*(S_2)/k_B$, where Eq. (9) is evaluated numerically by the Newton method as implemented in the software package Mathematica. We observe that the fourth-order expansion of S_0^* provides accurate results for $-0.2 \lesssim S_2 \lesssim 0.5$ but fails for stronger ordering. Contrary, the asymptotic expression for $S_2 \rightarrow 1$ captures the strong decrease of entropy for strong alignment accurately for $S_2 \gtrsim 0.8$. The divergence of the entropy near planar ordering is accurately described by the asymptotic expression for $S_2 \lesssim -0.3$. Although Eq. (11) matches only the leading order term for small S_2 , the interpolation formula is found to provide a very good approximation over the whole admissible range $-1/2 \leq S_2 < 1$. If needed, even more accurate interpolation formulas can be obtained by matching the next orders in the regime of weak orientation.

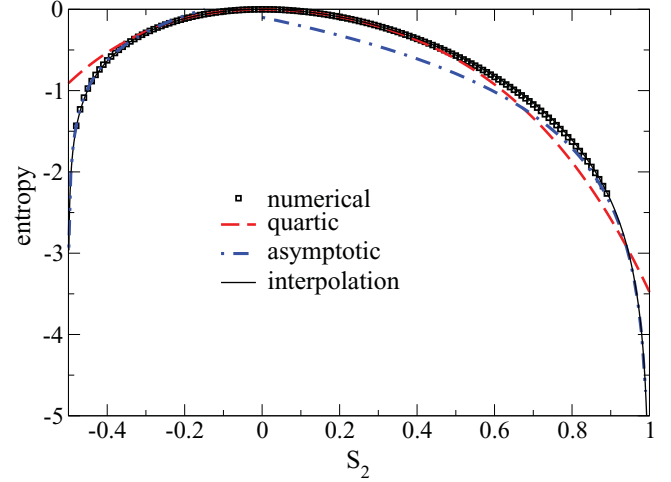


FIG. 1. (Color online) Squares show the dimensionless entropy S_0^*/k_B as a function of the order parameter S_2 for the case of uniaxial symmetry, Eq. (9). Shown are also the limiting cases for weak (dashed line) and strong (dot-dashed line) ordering; see Eq. (10). On this scale, the interpolation formula [Eq. (11)], shown as solid line, is indistinguishable from the numerical result of Eq. (9).

In the general case, the alignment tensor \mathbf{Q} shows not uniaxial but biaxial symmetry and is described by S_2 and an additional biaxiality parameter B_2 :

$$\mathbf{Q} = (S_2 + B_2/2)\mathbf{nn} + B_2\mathbf{mm} - (S_2/3 + B_2/2)\mathbf{1}. \quad (12)$$

The uniaxial case is recovered for $B_2 = 0$. In general, the directions perpendicular to \mathbf{n} are not equivalent and the parameter B_2 quantifies the ordering parallel to the second eigenvector \mathbf{m} of \mathbf{Q} (see, e.g., Ref. [29]). In Appendix B2, the special case $S_2 = 0, B_2 \neq 0$ is worked out and also there a logarithmic divergence near the fully ordered state is found, Eq. (B13). In the general case, $S_2 \neq 0, B_2 \neq 0$, we evaluate the entropy S_0^* numerically from Eqs. (7) and (6) for many different matrices \mathbf{A} . The upper half of Fig. 2 shows the numerical result of S_0^* plotted parametrically as a function of $S_2(\mathbf{A})$ and $B_2(\mathbf{A})$. We observe that S_0^* is symmetric in B_2 and therefore reserve the lower part of Fig. 2 for the fit function. The numerical results as well as the analytical result obtained in Appendix B2 suggest that the entropy decreases in a similar manner when S_2 or B_2 deviate from their zero equilibrium values. Therefore, we treat S_2 and B_2 on a similar footing in the desired expression for $S_0^*(S_2, B_2)$. Since B_2 is bounded by $|B_2| \leq \frac{2}{3}(1 - S_2) \leq 1$ [29], we introduce the scaled variable $\mathcal{B} = 1 - (3B_2/[2(1 - S_2)])^2$ which is bounded by $0 \leq \mathcal{B} \leq 1$.¹ We also introduce the quantity $\mathcal{S} = (1 + 2S_2)(1 - S_2)^2$, which is also restricted to the unit interval. Next, we make an ansatz of the form $S_0^*(S_2, B_2) = f(\mathcal{Q})$, with $\mathcal{Q} = \mathcal{S}\mathcal{B} = (1 + 2S_2)[(1 - S_2)^2 - (3B_2/2)^2]$. Instead of S_2, B_2 , it is common to use the two tensorial invariants I_2, I_3 of \mathbf{Q} . The invariants

¹From Eq. (12) follows a relation between the order parameters and the tensorial invariants (introduced later): $I_2 = (4S_2^2 + 3B_2^2)/12$ and $I_3 = 2S_2^2/27 - S_2B_2^2/6$, from which follows that the entropy and any scalar as function of the invariants is symmetric in B_2 .

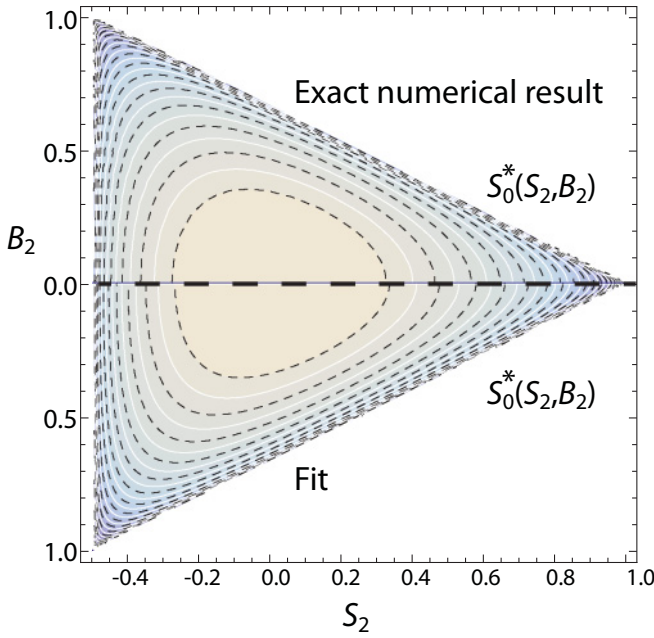


FIG. 2. (Color online) Contour plot of the dimensionless entropy S_0^*/k_B as a function of the order parameters S_2 and B_2 . The upper half shows the numerical result from Eq. (7) for many different matrices \mathbf{A} in Eq. (6). In the lower half, the entropy is evaluated from Eq. (13).

can be chosen as $I_2 = \frac{1}{2}\text{tr}(\mathbf{Q} \cdot \mathbf{Q})$ and $I_3 = \text{tr}(\mathbf{Q} \cdot \mathbf{Q} \cdot \mathbf{Q}) = 3 \det(\mathbf{Q})$, while $I_1 = \text{tr}(\mathbf{Q}) = 0$ by construction. In terms of the invariants, we find $\mathcal{Q} = 1 + 9(I_3 - I_2)$. A simple-fit function that reproduces the leading term in the known limiting cases is given by

$$S_0^*(\mathbf{Q})/k_B = \ln(\sqrt{\mathcal{Q}}) + \frac{2}{3}(\sqrt{\mathcal{Q}} - 1). \quad (13)$$

As seen from Fig. 2, the simple form of Eq. (13) reproduces the numerical results rather accurately within the whole physically admissible domain. Indeed, Eq. (13) in its uniaxial limit reproduces the exact result and Eq. (11) to within 2% for $S_2 \in [-0.1, 0.6]$ and to within 11% for S_2 outside this range. It was noted in Ref. [31] that a term quadratic in the third invariant I_3 is needed to describe certain biaxial phases. Our Eq. (13) reduces for small values of the tensorial invariants to the (entropic contribution to the) sixth-order Landau-de Gennes expansion [31]:

$$S_0^*(I_2, I_3) = -\frac{15}{2}I_2 + \frac{15}{2}I_3 - 27I_2^2 + 54I_2I_3 + \frac{1215}{8}I_2^3 - 27I_3^2 + \dots \quad (14)$$

The Landau-de Gennes free energy contains additional terms describing effective interactions (e.g., nematic, see next section). It is interesting to note, however, that already the ideal entropic contribution contains all powers of the invariants with rather large prefactors, such that the sixth-order expansion might be of little practical use.

Eqs. (11) and (13) and their corresponding limiting cases (8) and (10) are the main result of this work. Note that these expressions are universal in the sense that they are independent of applied fields or specific interactions, since they

describe the contribution of orientational ordering to the ideal entropy.

IV. EXAMPLE APPLICATIONS

In the following, two examples are presented, in order to illustrate the usefulness of the main results of Eqs. (8) and (10).

A. Dilute suspension in magnetic field

In the presence of an external magnetic field \mathbf{H} , the rod-like particles attain induced magnetic moments, which lead to the energy contribution,

$$E[f] = -\frac{1}{2}\chi\mathbf{Q}:\mathbf{H}\mathbf{H}, \quad (15)$$

where χ is the susceptibility (more precisely: the diamagnetic anisotropy) and H denotes the magnitude of \mathbf{H} . The free-energy F^* is given by Eq. (2), where $S_{\text{ex}} = 0$ for noninteracting rods.

For weak fields $\chi H^2 \ll k_B T$, the induced ordering is given to leading order in the external field H by $\mathbf{Q} = (\chi/15k_B T)(\mathbf{H}\mathbf{H} - (1/3)H^2\mathbf{1}) + \dots$. Since the external field induces uniaxial ordering along the field direction $\mathbf{H} = H\mathbf{n}$, the order parameter is of the form $\mathbf{Q} = S_2(H)[\mathbf{n}\mathbf{n} - (1/3)\mathbf{1}]$, where

$$S_2(H) = \frac{1}{15}h^2 + \frac{1}{315}h^4 - \frac{1}{4725}h^6 + \dots, \quad (16)$$

with the dimensionless quadratic field strength $h^2 = \chi H^2/k_B T$. In the opposite case of a very strong external field, $h \gg 1$, the asymptotic expression for the entropy can be used, Eq. (10), and the approach to the fully oriented state is described by $S_2 = 1 - 3/h^2$.

For general values of H , the induced ordering $S_2(H)$ can be obtained from $\partial F^*/\partial S_2 = 0$, using the interpolation formula of Eq. (13):

$$\frac{h^2}{3} = \frac{S_2[3 + 2\sqrt{1 + 2S_2(1 - S_2)}]}{(1 + 2S_2)(1 - S_2)}. \quad (17)$$

Equation (17) gives $h^2(S_2)$, which implicitly defines $S_2(h^2)$. Unfortunately, the explicit expression for the latter is rather lengthy. As expected, S_2 increases monotonically with h . The expansion of Eq. (16) gives accurate values for $h \lesssim 2$, where it deviates by 5%, whereas already for $h \gtrsim 4$, the asymptotic expansion is accurate to better than 2%.

B. Isotropic-nematic transition in liquid crystals

On a mean-field level, Maier and Saupe proposed an account of effective interactions between particles in a mean-field manner [1,32]:

$$E = -\frac{3}{4}k_B T U \mathbf{Q}:\mathbf{Q}, \quad (18)$$

where T is the temperature and U denotes the dimensionless interaction strength, which is a decreasing function of the molecular volume. On the macroscopic level, the free-energy functional Eq. (2) from Maier-Saupe interactions Eq. (18) and

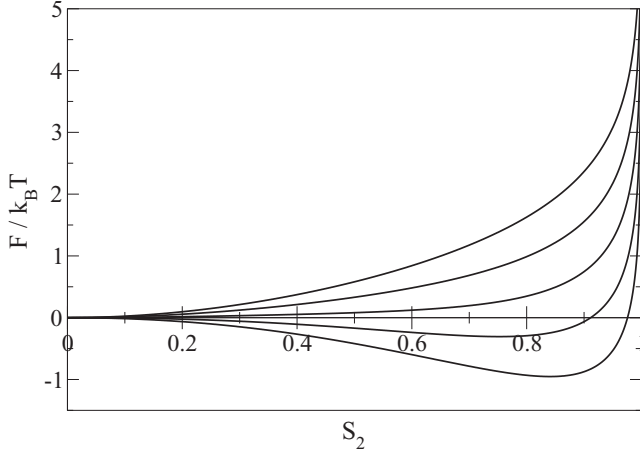


FIG. 3. The dimensionless Landau-de Gennes free-energy $F^*/k_B T$ as a function of the order parameter S_2 , Eq. (20). From top to bottom, the strength of the Maier-Saupe interaction energy, Eq. (18), increases as $U = 0, 2, 4, 6, 8$.

the ideal entropy Eq. (8) results in the Landau-de Gennes free energy:

$$F^*/k_B T = \frac{3}{4}(5 - U) \text{tr}(\mathbf{Q} \cdot \mathbf{Q}) - \frac{75}{14} \text{tr}(\mathbf{Q} \cdot \mathbf{Q} \cdot \mathbf{Q}) + \frac{3825}{784} [\text{tr}(\mathbf{Q} \cdot \mathbf{Q})]^2 + \mathcal{O}(\mathbf{Q}^5). \quad (19)$$

For $U < U^* = 5$, the isotropic state with $\mathbf{Q} = 0$ is stable but loses its stability at U^* . The same conclusions have been obtained in Ref. [33] from an independent stability analysis. Equation (19) is the classical Landau-de Gennes form of the free energy with correct tensor structure. Same as in classical Landau theory but different to the result [12], only the coefficient of quadratic term changes sign at transition, while the other coefficients are constant. In fact, the suspicious appearance of the Maier-Saupe interaction strength U in the cubic and quartic terms in [12] can be traced back to the decoupling approximation in the equations of motion.

It is important to keep in mind that Eq. (19) displays only the first terms of an expansion [1]. In order to discuss the isotropic-nematic transition, we resort to the full expression of Eq. (11), $F^*/k_B T = -\frac{1}{2} U S_2^2 - S_0^*/k_B$. The behavior of the Landau-de Gennes free energy [Eq. (20)] is shown in Fig. 3. The familiar scenario of a first-order phase transition is evident. Note, however, that F^* diverges for $S_2 \rightarrow 1$ (and $S_2 \rightarrow -1/2$), which guarantees that the order parameter stays within the physically admissible range. Obviously, such a restriction is absent in the fourth-order expansion.

In order to discuss the isotropic-nematic phase transition in more detail, one needs to find the minima of F^* . Thanks to the simple form of F^* , one finds that $S_2 = 0$ is always an extremum of $F^*(S_2)$, becoming a maximum instead of a minimum for $U > U^* = 5$. A second minimum of F^* arises at $U \geq U_c$. The governing quartic equation resulting from inserting Eq. (11) in $dF^*/dS_2 = 0$ is, however, difficult to study analytically. Since nematics order typically parallel to the director, the planarly ordered state does not play a crucial role. Therefore, a simpler entropy function than (11) can be employed that does not include the pole at $S_2 \rightarrow -1/2$. Ensuring the correct limiting

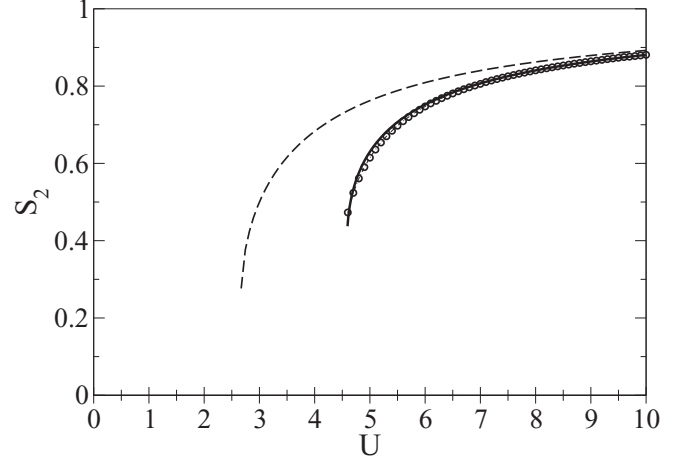


FIG. 4. The orientational order parameter S_2 as a function of the dimensionless interaction strength U of the Maier-Saupe potential, Eq. (18). Solid line shows the result of Eq. (21), whereas the dashed line is the result of Ref. [5]. Symbols denote the result from direct numerical solution of the self-consistency relation.

behavior at weak ordering and near the fully aligned state, the corresponding free energy with Maier-Saupe interaction reads

$$F^*/k_B T = -\frac{U}{2} S_2^2 - S_2(1 - S_2)^2 - \ln(1 - S_2) - S_2^3(1 - \ln 3). \quad (20)$$

This free-energy function is very similar to the one resulting from Eq. (11), and Eq. (13) also has $S_2 = 0$ as extremum, which at $U > U^*$ becomes a maximum instead of a minimum. The second minimum of F^* for $U \geq U_c$ is described by

$$S_2(U) = \frac{1}{6(2 - \ln 3)} \left[10 - 3 \ln 3 - U + \sqrt{U^2 + 2(2 - 3 \ln 3)U + 9(\ln 3)^2 - 20} \right], \quad (21)$$

where $U_c = 2\sqrt{3(2 - \ln 3)} + 3 \ln 3 - 2 \approx 4.5847$ is the location of the isotropic-nematic phase transition. The value of the order parameter at the transition $S_2(U_c) = 1 - [6 - 3 \ln 3]^{-1/2} \approx 0.39188$. Figure 4 shows that the values obtained here are very close to those obtained from directly solving the self-consistency relation $S_2 = \int d^2 u P_2(\mathbf{u} \cdot \mathbf{n}) e^{U S_2 P_2(\mathbf{u} \cdot \mathbf{n})} / Z$, where Z denotes the partition function $Z = \int d^2 u e^{U S_2 P_2(\mathbf{u} \cdot \mathbf{n})}$. The latter values are $U_c \approx 4.54$ and $S_2(U_c) \approx 0.43$ [1,32]. Due to decoupling approximations, the results obtained in Ref. [5], $U_c = 8/3$ and $S_2(U_c) = 1/4$, deviate considerably from the exact values.

It should be noted that, in general, the excess entropy due to excluded volume interactions [17] should be added to the free energy of Eq. (20), which will bring additional nonlinear contributions to the effective free-energy F^* [18,19].

V. CONCLUSIONS

In this work, the macroscopic form of the ideal orientational entropy in terms of the order parameter is derived within the quasiequilibrium ensemble (which corresponds to the maximum entropy principle). The limiting cases of weak and strong orientational ordering are obtained exactly, Eqs. (8)

and (10). Approximate interpolation formulas are proposed, Eqs. (11) and (13), which are found to be quite accurate over the whole range. While the orientational entropy shows the expected fourth-order expansion near the isotropic state, the entropy diverges logarithmically near the fully oriented phase, thereby assuring that the order parameter always stays within the physically admissible range. When combined with the Maier-Saupe potential, the present approach accurately predicts the isotropic-nematic phase transition and provides analytical expressions for the critical point.

The present results can also be extended for spatially inhomogeneous systems, where the Landau-de Gennes potential is augmented by so-called Frank-elastic terms [1,20,21,28,34].

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APPENDIX A: FAMILY OF TEST FUNCTIONS

Onsager proposed [17] the one-parametric family of test functions:

$$f_a(\mathbf{u}) = \frac{a}{4\pi \sinh(a)} \cosh(a\mathbf{u} \cdot \mathbf{n}). \quad (\text{A1})$$

He noted that the Bingham distributions of Eq. (5) provide a more realistic description. However, the family of Eq. (A1) is easier to handle analytically but still encompasses the isotropic ($a = 0$) as well as the fully oriented ($a \rightarrow \infty$) state. Evaluating the order parameter of Eq. (3) with Eq. (A1) gives $S_2 = 1 - 3 \coth(a)/a + 3/a^2$ and the entropy functional of Eq. (1) becomes the function

$$S_0(a) = \ln[a \coth(a)] - 1 + \tan^{-1}[\sinh(a)]/\sinh(a). \quad (\text{A2})$$

APPENDIX B: CUMULANT-GENERATING FUNCTION

From the definition of the generating function [Eq. (6)], expand in power series

$$G(\mathbf{A}) = \ln \sum_{n=0}^{\infty} \frac{1}{n!} K_n(\mathbf{A}), \quad (\text{B1})$$

where

$$K_n(\mathbf{A}) = \frac{1}{4\pi} \int d^2u (\mathbf{u} \cdot \mathbf{A} \cdot \mathbf{u})^n. \quad (\text{B2})$$

For symmetric second-rank tensor \mathbf{A} , the first integrals read $K_0 = 1, K_1 = t_1/3$,

$$\begin{aligned} K_2 &= \frac{1}{15} (t_1^2 + 2t_2), \\ K_3 &= \frac{1}{105} (t_1^3 + 6t_1t_2 + 8t_3), \\ K_4 &= \frac{1}{105} \left(t_1^4 + 4t_2^2 - 4t_1^2t_2 + \frac{32}{3}t_1t_3 \right), \end{aligned} \quad (\text{B3})$$

where $t_n = \text{tr}(\mathbf{A}^n)$. In the generating function, it is important to keep terms proportional to t_1 since $\partial t_1/\partial \mathbf{A} = \mathbf{1}$. With these integrals, the first terms of the expansion read

$$\begin{aligned} G(\mathbf{A}) &= \frac{1}{3}t_1 + \frac{1}{15} \left(t_2 - \frac{1}{3}t_1^2 \right) + \frac{4}{315} \left(t_3 - t_2t_1 + \frac{2}{9}t_1^3 \right) \\ &\quad - \frac{1}{1575} \left(t_2 - \frac{1}{3}t_1^2 \right)^2 + \dots \end{aligned} \quad (\text{B4})$$

From $G(\mathbf{A})$, the order parameter tensor is derived via differentiation,

$$\mathbf{Q} = \frac{2}{15}\mathbf{A} + \frac{4}{105} \overline{\mathbf{A} \cdot \mathbf{A}} - \frac{4}{1575} \text{tr}(\mathbf{A} \cdot \mathbf{A})\mathbf{A} + \dots \quad (\text{B5})$$

Here, we introduced the notation $\overline{\mathbf{X}} = \mathbf{X} - \frac{1}{3}\text{tr}(\mathbf{X})\mathbf{1}$ for the traceless part of a matrix \mathbf{X} . Expressing \mathbf{A} as a series expansion in \mathbf{Q} , $\mathbf{A} = c_1\mathbf{Q} + c_2\overline{\mathbf{Q} \cdot \mathbf{Q}} + \dots$, one finds from Eq. (B5)

$$\begin{aligned} \mathbf{A} &= \frac{15}{2}\mathbf{Q} - \frac{225}{14} \overline{\mathbf{Q} \cdot \mathbf{Q}} + c_3 \overline{\mathbf{Q} \cdot \mathbf{Q} \cdot \mathbf{Q}} \\ &\quad + c_4 \text{tr}(\mathbf{Q} \cdot \mathbf{Q})\mathbf{Q} + \dots, \end{aligned} \quad (\text{B6})$$

where $c_3 = 3825/98 - 2c_4$, and the representation of the third-order term is not unique.

1. Uniaxial symmetry

For uniaxial symmetry, $\mathbf{A} = a[\mathbf{nn} - (1/3)\mathbf{1}]$, the cumulant-generating function becomes

$$G_{\text{uni}}(a) = \ln \frac{1}{4\pi} \int d^2u e^{a[(\mathbf{n}\cdot\mathbf{u})^2 - 1/3]}. \quad (\text{B7})$$

Without loss of generality, choose \mathbf{n} as the z -axis of a spherical coordinate system. Then, the remaining integral in Eq. (B7) can be evaluated to give

$$G_{\text{uni}}(a) = -\frac{a}{3} + \ln \left[\frac{1}{2} \sqrt{\frac{\pi}{a}} \text{erfi}(\sqrt{a}) \right]. \quad (\text{B8})$$

The imaginary error function $\text{erfi}(\sqrt{a}) = \text{erf}(i\sqrt{a})/i$ can be expressed as $\text{erfi}(\sqrt{a}) = -a \int_0^{|a|} dz \exp(z)/\sqrt{\pi a^2 z}$. Note that G_{uni} can equivalently be expressed in terms of the Dawson function $D(x) = e^{-x^2} \int_0^x dt e^{t^2}$, but it is obvious from our rewriting of Eq. (B8) that G_{uni} is real for positive and negative values of a . From the generating function, the order parameter can be obtained by differentiation, $\mathbf{Q} = \partial G/\partial \mathbf{A}$. In the uniaxial case, this relation reads $S_2(a) = (3/2)G'_{\text{uni}}(a)$. From Eq. (B8), we obtain the expression

$$S_2(a) = \frac{3e^a}{2\sqrt{a\pi} \text{erfi}(\sqrt{a})} - \frac{3}{4a} - \frac{1}{2}, \quad (\text{B9})$$

from which the asymptotic expressions can be derived

$$S_2(a) = \begin{cases} \frac{2}{15}a + \frac{4}{315}a^2 + \mathcal{O}(a^3), & \text{as } a \rightarrow 0 \\ 1 - \frac{3}{2a} - \frac{3}{4a^2} + \mathcal{O}(1/a^3), & \text{as } a \rightarrow \infty \\ -\frac{1}{2} - \frac{3}{4a} + \mathcal{O}(e^a), & \text{as } a \rightarrow -\infty. \end{cases} \quad (\text{B10})$$

Reverting these equation in order to express $a(S_2)$ gives

$$a = \begin{cases} \frac{15}{2}S_2 - \frac{75}{14}S_2^2 + \dots, & \text{as } S_2 \rightarrow 0 \\ \frac{3}{2(1-S_2)} + \frac{1}{2} + \dots, & \text{as } S_2 \rightarrow 1 \\ -\frac{3}{4(S_2+1/2)}, & \text{as } S_2 \rightarrow -1/2. \end{cases} \quad (\text{B11})$$

2. Perfect biaxial symmetry

As a symmetric traceless tensor, \mathbf{A} can always be represented as $\mathbf{A} = (a + b/2)\mathbf{nn} + b\mathbf{mm} - (a/3 + b/2)\mathbf{1}$, where the director \mathbf{n} has already been introduced above. For biaxial ordering, the two directions perpendicular to \mathbf{n} are not equivalent. Thus, the second eigenvector \mathbf{m} appears in the representation of \mathbf{A} [29]. The uniaxial case considered above is obtained for $b = 0$. Here, we consider the other extreme case $a = 0$, which implies $S_2 = 0$. Then, the generating function of Eq. (6) can be evaluated analytically to give

$$G_{\text{biax}}(b) = \ln {}_1F_2\left(\frac{1}{2}; \frac{3}{4}, \frac{5}{4}; \frac{b^2}{16}\right), \quad (\text{B12})$$

where ${}_1F_2$ denotes the hypergeometric function. From $\mathbf{Q} = \partial G/\partial \mathbf{A}$, one obtains $\mathbf{Q} = (B_2/2)\mathbf{nn} + B_2\mathbf{mm} - (B_2/2)\mathbf{1}$, where the biaxiality parameter B_2 is given by $B_2 = 2G'_{\text{biax}}(b)$. Since the general case of weak ordering has already been worked out, Eq. (8), we focus on the case $a = 0$, $b \gg 1$ (“perfect biaxial ordering”). From the asymptotic expansion of the hypergeometric function, we obtain $G_{\text{biax}}(b) \approx |b|/2 - \ln|b| - \frac{1}{2}\ln(2) + \dots$ for $b \rightarrow \pm\infty$, and in this limit, therefore, $B_2 = (|b| - 2)/b + \dots$ or $b \approx 2/(1 - |B_2|)$. The Legendre transform [Eq. (7)] here reads $S_0^*/k_B = -bG'_{\text{biax}}(b) + G_{\text{biax}}(b)$ and becomes upon inserting the asymptotic expressions for perfect biaxial ordering

$$S_{0,\text{biax}}^*(B_2)/k_B = \ln(1 - |B_2|) + \frac{1 - B_2}{1 - |B_2|} - \frac{3}{2}\ln(2) + \dots \quad (\text{B13})$$

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