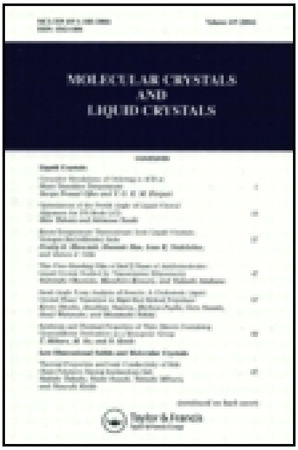

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C. Papenfuss [a] & W. Muschik [a]

[a] Institut für Theoretische Physik, Technische Universität, Berlin

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Orientational Order in Free Standing Liquid Crystalline Films and Derivation of a Closure Relation for Higher Order Alignment Tensors

C. PAPENFUSS and W. MUSCHIK

Institut für Theoretische Physik, Technische Universität Berlin

The orientational ordering present in all liquid crystalline phases is described by an anisotropic orientation distribution function (ODF), which depends on position, time and the particle orientation. Besides the ODF other mesoscopic fields, depending on the same set of variables, are introduced, and balance equations for them are given. The mesoscopic balance of spin and the mesoscopic balance of mass together yield a differential equation for the ODF and for its second moment, the alignment tensor in the presence of an electric field. Because higher order alignment tensors enter into the equation for the second order one a closure relation, expressing them in terms of the second order one, is needed. Such a closure relation is derived from the principle of maximum entropy.

MESOSCOPIC CONCEPT

Liquid crystals consist of non-spherical particles. Here it is assumed that the particles are rotational symmetric with axis of rotation called microscopic director $\underline{n}$. In all liquid crystalline phases the microscopic directors exhibit a long range orientational order, which can be described introducing an orientation distribution function (ODF).

This distribution function is defined on the so called nematic space, spanned by position $\underline{x}$, orientation $\underline{n}$, and time t. The anisotropic moments of the ODF are called alignment tensors

$$a^{(k)} := \int_{S^2} f(\underline{x}, \underline{n}, t)\, \underbrace{\overline{\underline{n} \ldots \underline{n}}}_{k}\, d^2 n \quad , \tag{1}$$

where $\overline{\cdots}$ denotes the symmetric irreducible part of a tensor. Because of the symmetry of the ODF $f(-\underline{n}) = f(\underline{n})$ only even order alignment tensors are nonzero. If the ODF is uniaxial, the alignment tensors can be expressed with order parameters $S^{(k)}$ and the macroscopic director (the axis of rotation symmetry of the ODF):

$$a^{(k)} = S^{(k)}\, \underbrace{\overline{\underline{d} \ldots \underline{d}}}_{k} \quad . \tag{2}$$

for symmetry reasons. The second order parameter S is the Maier-Saupe order parameter.

The idea of the mesoscopic theory is to define fields on a higher dimensional domain (the nematic space), in contrast to the Ericksen-Leslie theory, which introduces an additional macroscopic field (the macroscopic director $\underline{d}$). So called mesoscopic fields are introduced, depending not only on position and time, but also on the microscopic director (the orientation). For instance the mesoscopic mass density $\hat{\rho}(\underline{x}, \underline{n}, t)$ is the mass density of particles of the particular orientation $\underline{n}$. Mesoscopic fields are denoted with a ˆ. Macroscopic fields are obtained from mesoscopic ones by avaraging with the ODF.

The example we are mainly interested in is a thin film with a rotating electric field applied to it. The thin film can be approximated by a mathematical surface, and the balance equations for such two dimensional systems have been derived in [1]. For instance the balance equation for the surface mass density reads

$$\frac{\partial}{\partial t}\rho_s - 2\rho_s K_M w^{\perp} + (\rho_s w^{\alpha})_{;\alpha} = -[\![\rho(v^m - w^m)]\!] e_m \quad . \tag{3}$$

where ρ_s is the surface mass density, K_M the mean surface curvature, $\underline{w}$ the surface velocity, and $[\![\ \ ]\!]$ denotes the difference of the limiting values of the bulk fields on both sides of the surface. Compared to the mass balance in the bulk the gradient is replaced by the covariant surface derivative, and additional terms involving the surface velocity and the mean curvature appear. However from experiments it is known that free standing films are flat to a very high accuracy. and if the film is at rest, equation (3) reduces to the well known continuity equation. For a flat film at rest similiarly all other balance equations have the same form as in the bulk. These equations will be used here, but they would not be apropriate to describe a moving curved surface, like for instance a phase boundary.

For the mesoscopic quantities balance equations have been derived [2, 3]. From the mesoscopic balance of mass one has for the ODF in the case of an incompressible fluid [4]:

$$\frac{\partial f}{\partial t} + \underline{\hat{v}} \cdot \nabla f + \nabla_n \cdot (\underline{u} f) = 0 \quad . \tag{4}$$

$\underline{\hat{v}}$ is the material velocity of particles of orientation $\underline{n}$. $\underline{u}$ is the orientation change velocity. It is tangential to the unit sphere. ∇_n denotes the covariant derivative with respect to the orientation variable. The last term on the left hand side of eq. (4) is the flux in orientation space. It expresses the fact that the fraction of particles of orientation $\underline{n}$ changes if the particles change their orientation.

THE ORIENTATION CHANGE VELOCITY AND THE ALIGNMENT TENSOR

A derivation of an equation for the orientation change velocity has been presented in a previous paper [4], [5], and the results will be summarized here only. In the present paper we focus mainly on the derivation of a closure relation for the higher order alignment tensors in terms of the second order one.

The mesoscopic balance of spin reads:

$$\frac{\partial \hat{\rho} \underline{\hat{s}}}{\partial t} + \nabla \cdot \left(\hat{\rho} \underline{\hat{v}} \underline{\hat{s}} - \left(\underline{n} \times \underline{\underline{\hat{\Pi}}} \right)^T \right) + \nabla_n \cdot (\hat{\rho} \underline{u} \underline{\hat{s}}) = \underline{\underline{\underline{\epsilon}}} : \underline{\underline{\hat{t}}} + \hat{\rho} \underline{n} \times \underline{\hat{g}} \quad . \tag{5}$$

The symbols are: $\underline{\hat{s}}$: mesoscopic specific spin density, $\underline{\underline{\hat{\Pi}}}$: couple stresses ($\nabla \cdot \underline{\underline{\hat{\Pi}}}$ are short range forces acting on the orientation), $\underline{\underline{\hat{t}}}$: mesoscopic stress tensor, $\underline{\hat{g}}$: couple forces (long range forces acting on the orientation). Together with the relation $\underline{s} = \theta \underline{n} \times \underline{u}$ this is a differential equation for the orientation change velocity. The following simplifications

1. The spin is stationary: $\frac{\partial \hat{s}}{\partial t} = 0$.

2. There is no material flux: $\underline{\hat{v}} \equiv 0$. In the case of free standing liquid crystalline films in a rotating electric field there are experimental hints that there is no flow of material [6].

make an algebraic equation for $\underline{u}$ out of it. $\underline{\underline{\hat{t}}}$, $\underline{\underline{\hat{\Pi}}}$ and $\underline{\hat{g}}$ are constitutive quantities. They depend on the variables in the state space in a material dependent manner. The set of variables for the constitutive quantities is chosen as

$$Z = \left(\hat{\rho}, T, \underline{E}, \underline{\underline{a}}, \nabla\underline{\underline{a}}, \nabla\nabla\underline{\underline{a}}, \frac{\nabla\hat{\rho}}{\hat{\rho}}, \frac{\nabla\nabla\hat{\rho}}{\hat{\rho}}, \frac{\nabla_n\hat{\rho}}{\hat{\rho}}, \underline{n}\right) \quad , \tag{6}$$

(T: temperature), including the electric field $\underline{E}$ and spatial gradients because orientation patterns are inhomogenuous in space. Then a representation theorem linear in all derivatives and quadratic in $\underline{E}$ gives ($\underline{\underline{P}} =: \underline{\underline{\delta}} - \underline{nn}$)

$$\begin{aligned}\underline{u} = \beta_3 \nabla_n \ln\hat{\rho} + \underline{\underline{P}} \cdot \Bigg(\beta_5\underline{\underline{a}} + \beta_6\underline{\underline{a}} \cdot \underline{\underline{a}} + \beta_9\underline{\underline{a}} \cdot \underline{nn} \cdot \underline{\underline{a}} + \beta_7\underline{EE} + \\ + \beta_8\underline{nn} : \nabla\nabla\underline{\underline{a}} + \beta_{10}\frac{\nabla\nabla\hat{\rho}}{\hat{\rho}} + \beta_{11}\underline{n} \cdot \nabla\nabla\underline{\underline{a}} \cdot \underline{n} + \beta_{12}\underline{nn} : \underline{\underline{aa}}\Bigg) \cdot \underline{n} \quad .\end{aligned} \tag{7}$$

The coefficients β_j are functions of the macroscopic mass density $\rho(\underline{x}, t)$ and the temperature $T(\underline{x}, t)$.

The second tensorial irreducible moment of eq. (4) reads

$$\frac{\partial}{\partial t}\int_{S^2} f\ \overline{\underline{nn}}\ d^2n + \underline{v} \cdot \nabla \int_{S^2} f\ \overline{\underline{nn}}\ d^2n + \int_{S^2} \overline{\underline{nn}}\ \nabla_n \cdot (f\underline{u}) d^2n = 0 \quad . \tag{8}$$

and inserting $\underline{u}$ we obtain:

$$\begin{aligned}\frac{\partial\underline{\underline{a}}}{\partial t} = 6\beta_3\underline{\underline{a}} + 2\beta_{10}\left(\nabla\nabla \cdot \underline{\underline{a}}\right)^{symm} + \left(\left(\underline{\underline{a}} + \frac{1}{3}\underline{\underline{\delta}}\right) \cdot \underline{\underline{A}}\right)^{symm} - \\ -2\left(\underline{\underline{A}} + \beta_{10}\nabla\nabla\right) : \int_{S^2} \underline{nnnn} f d^2n + 2\left(\underline{\underline{\underline{B}}} : \cdot \int_{S^2} \underline{nnnn} f d^2n\right)^{symm} - \\ -2\left((\beta_8 + \beta_{11})\nabla\nabla\underline{\underline{a}} + \beta_{12}\underline{\underline{aa}}\right) :: \int_{S^2} \underline{nnnnnn} f d^2n \quad ,\end{aligned} \tag{9}$$

where $(\ldots)^{symm}$ denotes the symmetric part of a tensor, and we have introduced $\left(\nabla\nabla\underline{\underline{a}}\right)^T_{ijkl} := \nabla_k\nabla_l a_{ij}$. We have introduced the abreviations $\underline{\underline{A}} := \beta_5\underline{\underline{a}} + \beta_6\underline{\underline{a}} \cdot \underline{\underline{a}} + \beta_7\underline{EE}$, $\underline{\underline{\underline{B}}} = \left(\beta_8\left(\nabla\nabla\underline{\underline{a}}\right)^T + \beta_{11}\nabla\nabla\underline{\underline{a}} + \beta_{12}\underline{\underline{aa}}\right)$ Equation (9) is the differential equation for the second order alignment tensor, but it is not a closed equation due to the appearance of the higher moments $\int_{S^2} \underline{nnnn} f d^2n$ and $\int_{S^2} \underline{nnnnnn} f d^2n$. A closure relation expressing them in terms of the second order alignment tensor is needed.

DERIVATION OF A CLOSURE RELATION FOR THE HIGHER MOMENTS

In order to derive a closure relation we go back to the microscopic level, i.e. to a description on the phase space.

The well known equilibrium phase space distribution functions, the canonical and grand canonical one, are the phase space distribution functions, which maximize the entropy $\int_\Gamma f \ln f d\Gamma$ compared to all other distribution functions giving the same prescribed values for the avarage energy or for the avarages of energy and particle number, respectively. Jaynes [7] has generalized this to nonequilibrium taking into account constraints not only on the equilibrium variables. This principle of maximum entropy has been widely applied in the statistical foundation of Extended Thermodynamics [8] as well as in other branches of non-equilibrium thermodynamics [9].

The Γ-space for N uniaxial particles is spanned by the positions of the particles $\underline{x}_1 \cdots \underline{x}_N$, their orientations $\underline{n}_1 \cdots \underline{n}_N$ and the respective velocities $\dot{\underline{x}}_1 \cdots \dot{\underline{x}}_N$, $\dot{\underline{n}}_1 \cdots \dot{\underline{n}}_N$ with $\underline{x}_i \in \mathbb{R}^3$, $\underline{n}_i \in S^2$, $\dot{\underline{x}}_i \in \mathbb{R}^3$ and $\dot{\underline{n}}_i \in T_{\underline{n}}S^2$ for $i \in \{1, \ldots, N\}$. $\bar{\Gamma}$ denotes the coordinates in Γ-space:

$$d\bar{\Gamma} = \frac{1}{N!h^{5N}} d\underline{x}_1 \ldots d\underline{x}_N d\dot{\underline{x}}_1 \ldots d\dot{\underline{x}}_N d\underline{n}_1 \ldots d\underline{n}_N d\dot{\underline{n}}_1 \ldots d\dot{\underline{n}}_N \tag{10}$$

For the fields of mass density, energy density, momentum density, spin density and alignment tensor corresponding Γ-space observables are introduced. They are denoted by "~".

$$\begin{aligned}
\tilde{\rho}(\bar{\Gamma}; \underline{x}) &= \sum_{\alpha=1}^{N} m\delta(\underline{x} - \underline{x}^\alpha) \quad . \quad \tilde{\rho}\tilde{\underline{v}}(\bar{\Gamma}; \underline{x}) = \sum_{\alpha=1}^{N} m\dot{\underline{x}}^\alpha \delta(\underline{x} - \underline{x}^\alpha) \quad , & (11) \\
\tilde{\rho}\tilde{e}(\bar{\Gamma}; \underline{x}) &= \sum_{\alpha=1}^{N} \left(\frac{m}{2}\dot{\underline{x}}^\alpha \cdot \dot{\underline{x}}^\alpha + \frac{\theta}{2}\dot{\underline{n}}^\alpha \cdot \dot{\underline{n}}^\alpha + e_0(\underline{x}^\alpha) + \underline{\underline{\epsilon}}_1(\underline{x}^\alpha) : \overline{\underline{n}^\alpha \underline{n}^\alpha} + \underline{\underline{\epsilon}} : \underline{EE} \right) \delta(\underline{x} - \underline{x}^\alpha) & (12) \\
\tilde{\rho}\tilde{\underline{s}}(\bar{\Gamma}; \underline{x}) &= \sum_{\alpha=1}^{N} \theta \underline{n}^\alpha \times \dot{\underline{n}}^\alpha \delta(\underline{x} - \underline{x}^\alpha) \quad . \quad \tilde{\rho}\tilde{\underline{\underline{a}}}(\bar{\Gamma}; \underline{x}) = \sum_{\alpha=1}^{N} m \, \overline{\underline{n}^\alpha \underline{n}^\alpha} \, \delta(\underline{x} - \underline{x}^\alpha) & (13)
\end{aligned}$$

and similarly for the higher order alignment tensors. N is the total number of particles, and m the particle mass. Note that these observables depend on the

Γ-space coordinates and on the position $\underline{x}$ in the continuum. The δ-distribution in (11) to (13) "counts" only the particles, which are in the continuum element around $\underline{x}$. $\underline{\underline{e}}_1 : \overline{\underline{n}\underline{n}}$ is the anisotropic part of the mean field energy of one particle in the potential of the others.

We are looking for the most probable phase space distribution function $f^\Gamma(\bar{\Gamma}, t)$, which gives the correct macroscopic fields $\langle\tilde{\rho}\rangle = \rho(\underline{x}, t), \langle\tilde{e}\rangle = e(\underline{x}, t)$, $\langle\underline{\tilde{v}}\rangle = \underline{v}(\underline{x}, t)$, $\langle\underline{\tilde{s}}\rangle = \underline{s}(\underline{x}, t)$, $\langle\underline{\tilde{a}}\rangle = \underline{a}(\underline{x}, t)$ as averages of the corresponding phase space observables. Beside these constraints the phase space distribution function is supposed to maximize the entropy density (K: Boltzmann constant) [7]

$$s(\underline{x}, t) = -K \int_\Gamma \sum_{\alpha=1}^{N} f^\Gamma(\bar{\Gamma}, t) \ln f^\Gamma(\bar{\Gamma}, t) \delta(\underline{x} - \underline{x}^\alpha) d\bar{\Gamma} \quad . \tag{14}$$

The maximization of (14) with respect to f^Γ together with the normalisation results in

$$f^\Gamma_{max}(\bar{\Gamma}, t) \;=\; \frac{\exp\{-\frac{1}{K}\sum_A \int d^3r \lambda_A(\underline{r}) \tilde{u}_A(\bar{\Gamma}, \underline{r})\}}{\int_\Gamma \exp\{-\frac{1}{K}\sum_A \int d^3r \lambda_A(\underline{r}) \tilde{u}_A(\bar{\Gamma}, \underline{r})\} d\bar{\Gamma}} \quad , \tag{15}$$

where the Lagrange multipliers λ_A have been introduced to take into account the constraints. The orientation distribution function is defined as

$$f^{ODF}(\underline{x}, \underline{n}, t) = \frac{1}{\rho(\underline{x}, t)} \int_\Gamma \left(\sum_{\alpha=1}^{N} m f^\Gamma(\bar{\Gamma}, t) \delta(\underline{x} - \underline{x}^\alpha) \delta(\underline{n} - \underline{n}^\alpha) \right) d\bar{\Gamma} \quad . \tag{16}$$

The δ-distributions take into account only particles in the volume element around $\underline{x}$ and in the element around $\underline{n}$ in orientation space.

Inserting the phase space distribution function obtained from the maximum entropy principle one has after some manipulations:

$$f^{ODF}(\underline{x}, \underline{n}, t) = \frac{\exp -\underline{\underline{\Lambda}}(\underline{x}, t) : \overline{\underline{n}\underline{n}}}{\int_{S^2} \exp -\underline{\underline{\Lambda}}(\underline{x}, t) : \overline{\underline{n}\underline{n}} \; d^2n} = \frac{\exp\{-l\underline{dd} : \underline{nn}\}}{\int_{S^2} \exp\{-l\underline{dd} : \underline{nn} d^2n\}} \quad , \tag{17}$$

where the last identity applies to uniaxial phases only. The moments of this orientation distribution function can be calculated and the following parametric relation between the second and the fourth order parameter is obtained:

$$S \;=\; -\frac{3}{2} \frac{\frac{\partial}{\partial l}\left(2\pi^{3/2} \frac{Erf(\sqrt{l})}{\sqrt{l}}\right)}{\left(2\pi^{3/2} \frac{Erf(\sqrt{l})}{\sqrt{l}}\right)} - \frac{1}{2} \quad . \tag{18}$$

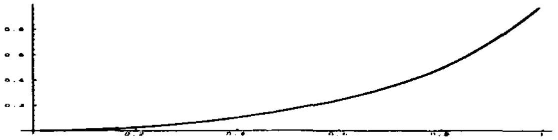

Figure 1: The dependence of the fourth order parameter S^4 on the second order parameter S

$$S^{(4)} = \frac{35}{8}\frac{\frac{\partial^2\left(2\pi^{3/2}\frac{Erf(\sqrt{l})}{\sqrt{l}}\right)}{\partial l^2}}{\left(2\pi^{3/2}\frac{Erf(\sqrt{l})}{\sqrt{l}}\right)} + \frac{15}{4}\frac{\frac{\partial\left(2\pi^{3/2}\frac{Erf(\sqrt{l})}{\sqrt{l}}\right)}{\partial l}}{\left(2\pi^{3/2}\frac{Erf(\sqrt{l})}{\sqrt{l}}\right)} + \frac{3}{8} \quad . \tag{19}$$

The result is shown in figure 1

Interestingly $S^{(4)}$ is always positive (see figure 1). This means that in the expansion of the ODF the contribution of the fourth order term is always a correction making the ODF more "δ-like".

CONCLUSIONS

Starting with the orientational balances we derived a differential equation for the orientation distribution function (ODF). The special form of this equation was obtained under several assumptions. Taking the second moment of this equation a nonlinear partial differential equation for the second order alignment tensor is obtained. The orientation distribution function is hardly experimentally accessable, and the second order alignment tensor is the most important quantity from the experimental point of view. The fourth and the sixth moment of the ODF enter into the equation for the second order alignment tensor. Closure relations expressing these higher moments in terms of the second one have been derived applying the principle of maximum entropy. We have seen that the principle of maximum entropy gives a universal relation between the fourth order parameter (and also for all higher order parameters) and the Maier-Saupe order parameter S. Universal means that the relation depends neither on variables like temperature nor on the material.

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