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MESOSCOPIC CONTINUUM THEORY FOR LIQUID CRYSTALS

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ABSTRACT. A summary of the mesoscopic theory of liquid crystals is presented. Mesoscopic field quantities are defined on the enlarged space of position, time and orientation. An orientation distribution function is defined as the fraction of the mesoscopic mass density over the total mass density. For the mesoscopic field quantities of mass, momentum, angular momentum and energy balance equations on the enlarged domain are formulated. They allow the derivation of a differential equation for the orientation distribution function. Measurable quantities are macroscopic ones. They are obtained from the mesoscopic quantities by averaging with the orientation distribution function. In addition to the usual macroscopic fields, alignment tensors are obtained by the averaging procedure. These tensors of successive order are a measure of the orientational order, present on the mesoscopic level. For these alignment tensors equations of motion are derived here. They form a set of coupled equations for infinitely many alignment tensors, and a closure is needed. At the lowest level, only the alignment tensor of second order is an independent variable, and the fourth order tensor is substituted by an algebraic closure relation. At this level of approximation Landau theory of phase transitions can be recovered in case of vanishing flow field. In a refined approach, the second and the fourth order alignment tensors are considered as independent variables, and the sixth order tensor is eliminated by an algebraic closure relation. This refined alignment tensor dynamics is considered in detail in the case of a uniaxial orientation distribution function.

1. Introduction

Polymers, micro-crystalline solids, ferro-fluids, liquid crystals, polymer melts, solids with micro-cracks and fiber suspensions are typical examples for materials with an internal structure. They show complex macroscopic material behavior, because the internal structure can change under the action of external fields. For instance, polymer melts show non-Newtonian rheological properties, due to stretching and reorientation of the polymer chains. The reorientation of micro-crystallites under deformation leads to material behavior, depending on the loading history. In ferro-fluids, the viscosity and other properties can be changed by a magnetic field. The interesting optical properties of liquid crystals, leading to many technical applications, are due to the orientational order of the non-spherical molecules.

There exist many different approaches towards a constitutive theory, and we have to distinguish between macroscopic (phenomenological) theories and theories with a more refined background. The macroscopic quantities of the phenomenological theories are directly measurable, whereas all other theories need some statistical averaging procedure. A wide field of statistical theories is based on the phase space, introducing interaction forces or potentials between molecules. Here, we will not deal with the microscopic background, but we are concerned with a phenomenological theory, the so called mesoscopic theory. This mesoscopic theory is between microscopic and macroscopic theories in the sense that no microscopic interactions between molecules are introduced; however, mesoscopic fields contain more information than the macroscopic ones. The idea is to enlarge the domain of the field quantities. The mesoscopic fields are defined on the space $\mathbb{R}^3_x \times \mathbb{R}_t \times M$. The manifold M is given by the set of values the internal degree of freedom can take. Therefore, the choice of M depends on the complex material under consideration.

Beyond the use of additional variables, the mesoscopic concept introduces a statistical element, the so-called *mesoscopic distribution function*. The macroscopic properties are the result of an averaging procedure with the distribution function.

The mesoscopic theory will be presented on the example of the alignment tensor theory of liquid crystals. Here, the additional degree of freedom is the orientation of a molecule, and the distribution function is an orientation distribution (see also Blenk *et al.* 1991; Muschik *et al.* 1996; Ehrentraut *et al.* 1997; Muschik *et al.* 2000; Papenfuss 2000; Muschik *et al.* 2004a,b).

2. Mesoscopic concept on the example of liquid crystals

2.1. Orientation distribution function. Liquid crystals consist of needle-shaped molecules. The microscopic director is defined as a unit vector pointing in the temporary direction of a needle-shaped rigid particle. The different particle orientations in the volume element give rise to an orientation distribution function $f(n,x,t)$, which is a uniform distribution in the isotropic phase and an inhomogeneous distribution in the liquid crystalline phase.

The aim is to introduce the orientation distribution function into a continuum description. Formally, the liquid crystal can be considered as a mixture of different chemical components, the components being distinguished by particle orientation. The component index is a continuous one, the microscopic director n. The mesoscopic field quantities depend on orientation n in addition to position and time. $\rho(n,x,t)$ for instance is the mass density "counting" only particles of orientation n. The mesoscopic mass density allows to define the orientation distribution (ODF) as the mass fraction of a particular orientation n:

$$f(n,x,t) = \frac{\rho(n,x,t)}{\rho(x,t)} \ . \tag{1}$$

2.2. Mesoscopic balance equations. Analogously to the case of mixture theory, we can formulate balance equations for a particular component, here for a particular orientation. These are the mesoscopic balance equations. Let us summarize the balance equations here. The derivative with respect to the mesoscopic variable microscopic director n is denoted by ∇_n. It is the covariant derivative on the unit sphere, and the orientation change velocity $u = \dot{n}$ is tangential to the unit sphere.

material	internal structure	Manifold $\mathcal{M}$
steel	orientation of crystal axes of micro-crystallites	$SO(3)$
shape memory alloys	fraction of different phases and orientation of crystal axes	$[0,1] \times SO(3)$
polymer solutions	orientation and length of end-to-end vector	$S^2 \times [0,r]$
liquid crystals of uniaxial molecules	orientation of particle = microscopic director	S^2
damaged material	size and orientation of micro-cracks	$\mathbb{R}^+ \times S^2$

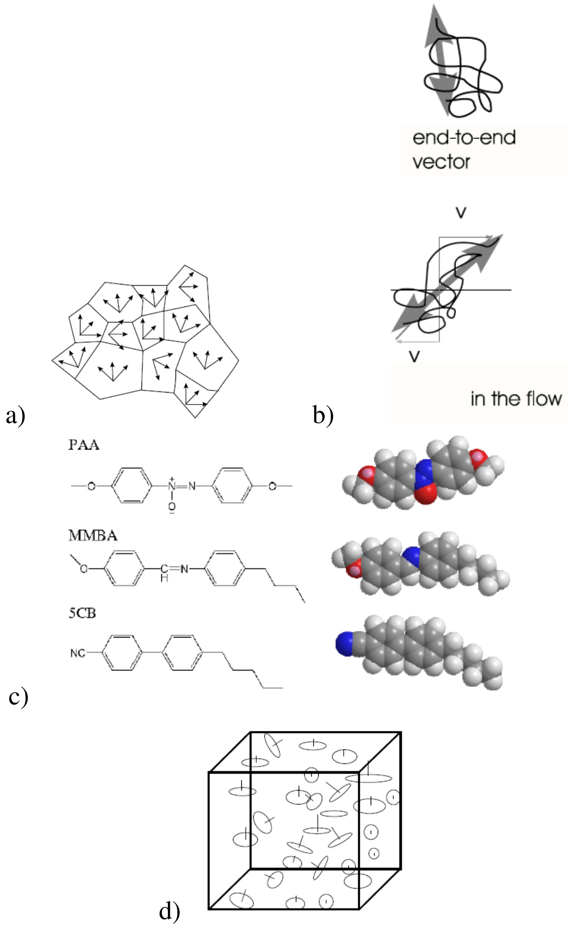


FIGURE 1. Examples of complex materials with corresponding choice of enlarged domain of field quantities: a) Microcrystallites in a polycrystal, b) end-to-end vector of a polymer molecule in a suspension at rest and in a flow field, c) examples of liquid crystal molecules and d) penny-shaped microcracks in a volume element.

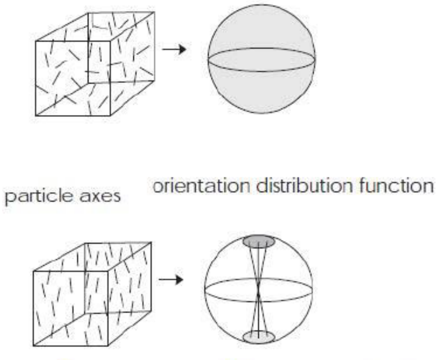


FIGURE 2. Orientation distribution function in the isotropic phase and in the liquid crystalline phase.

Mass

$$\frac{\partial}{\partial t}\rho(\cdot) \;+\; \nabla_x\cdot\{\rho(\cdot)v(\cdot)\}+\nabla_n\cdot\{\rho(\cdot)u(\cdot)\} \;=\; 0\,. \tag{2}$$

The last term shows that the density of particles of the particular orientation n may change due to rotation of particles with velocity u.

Momentum

$$\begin{aligned}\frac{\partial}{\partial t}[\rho(\cdot)v(\cdot)] \;&+\; \nabla_x\cdot\left[v(\cdot)\rho(\cdot)v(\cdot)-t^{\top}(\cdot)\right] \;+\\ &+\; \nabla_n\cdot\left[u(\cdot)\rho(\cdot)v(\cdot)-T^{\top}(\cdot)\right] \;=\; \rho(\cdot)g(\cdot).\end{aligned} \tag{3}$$

Here $\rho g(\cdot)$ is the external force density, $t^{\top}(\cdot)$ the transposed stress tensor, and $T^{\top}(\cdot)$ the transposed stress tensor on the unit sphere S^2, *i.e.*, the non-convective momentum flux on the unit sphere.

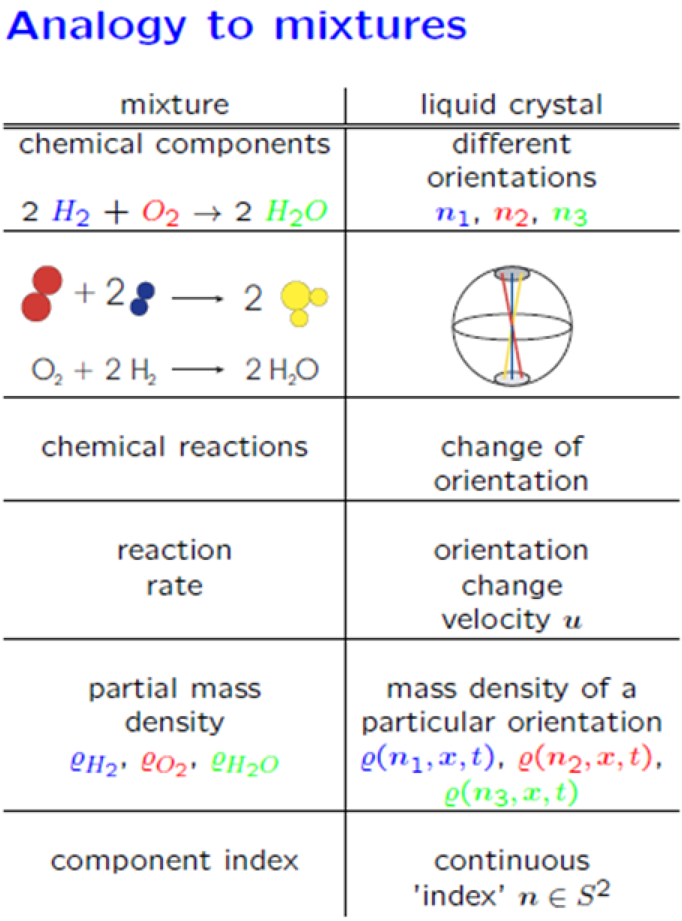
Angular Momentum

In addition, we have a balance of angular momentum, which is independent of the balance of momentum, due to rotations of the particles, which are not point like:

$$S(\cdot) := x\times v(\cdot)+s(\cdot), \tag{4}$$

$$\begin{aligned}\frac{\partial}{\partial t}[\rho(\cdot)S(\cdot)] \;&+\; \nabla_x\cdot\left[v(\cdot)\rho(\cdot)S(\cdot)-(x\times t(\cdot))^{\top}-\Pi^{\top}(\cdot)\right] \;+\\ &+\; \nabla_n\cdot\left[u(\cdot)\rho(\cdot)S(\cdot)-(x\times T(\cdot))^{\top}-W^{\top}(\cdot)\right] \;=\\ &=\; \rho(\cdot)x\times g(\cdot) \;+\; \rho(\cdot)m.\end{aligned} \tag{5}$$

Here s is the vector of the specific spin (internal angular momentum due to particle rotations), m the vector of volume torque density, the second order tensor Π is the surface torque (the non-convective flux of angular momentum in position space), and W is the analogue to Π with respect to the orientation variable n. All these quantities are mesoscopic ones,



Analogy to mixtures

mixture	liquid crystal
chemical components $2\ H_2 + O_2 \rightarrow 2\ H_2O$	different orientations $n_1,\ n_2,\ n_3$
$+\,2 \longrightarrow 2$ $O_2 + 2\,H_2 \longrightarrow 2\,H_2O$	
chemical reactions	change of orientation
reaction rate	orientation change velocity u
partial mass density $\varrho_{H_2},\ \varrho_{O_2},\ \varrho_{H_2O}$	mass density of a particular orientation $\varrho(n_1,x,t),\ \varrho(n_2,x,t),\ \varrho(n_3,x,t)$
component index	continuous 'index' $n \in S^2$

FIGURE 3. Analogy between mesoscopic theory and continuum theory of mixtures.

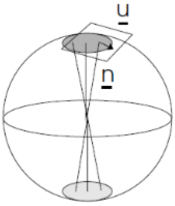


FIGURE 4. Orientation change velocity u

depending on position, time, and orientation. From the balance of total angular momentum, we can derive the balance of internal angular momentum, denoted as spin:

$$\begin{aligned} &\frac{\partial \rho(\cdot)s(\cdot)}{\partial t} + \nabla_x \cdot \left(\rho(\cdot)v(\cdot)s(\cdot) - \Pi(\cdot)^T\right) \\ &+\nabla_n \cdot \left(\rho(\cdot)u(\cdot)s(\cdot) - W^\top(\cdot)\right) = \varepsilon : t(\cdot) + \rho(\cdot)m(\cdot) \end{aligned} \tag{6}$$

with the totally antisymmetric, third order tensor ε.

Total Energy

$$e^{\text{tot}}(\cdot) := \frac{1}{2}v^2(\cdot) \;+\; \frac{1}{2}s(\cdot)\cdot\Theta^{-1}\cdot s(\cdot) \;+\; e(\cdot), \tag{7}$$

$$\begin{aligned} &\frac{\partial}{\partial t}[\rho(\cdot)e^{\text{tot}}(\cdot)] + \\ +\quad &\nabla_x \cdot \left[v(\cdot)\rho(\cdot)e^{\text{tot}}(\cdot) - t(\cdot)^\top \cdot v(\cdot) - \Pi(\cdot)^\top \cdot \Theta^{-1} \cdot s(\cdot) + q(\cdot)\right] + \\ +\quad &\nabla_n \cdot \left[u(\cdot)\rho(\cdot)e^{\text{tot}}(\cdot) - T(\cdot)^\top \cdot v(\cdot) - W(\cdot)^\top \cdot \Theta^{-1} \cdot s(\cdot) + Q(\cdot)\right] = \\ =\quad &\rho(\cdot)g \cdot v(\cdot) \;+\; \rho(\cdot)m(\cdot)\cdot\Theta^{-1}\cdot s(\cdot) + \rho(\cdot)r(\cdot). \end{aligned} \tag{8}$$

Here r is the absorption supply, Θ the moment of inertia tensor of the particles, q the heat flux density, and Q the heat flux density (the non-convective energy flux) on the unit sphere. Here again, all quantities are mesoscopic ones. depending on orientation, position and time.

2.3. Differential equation for the orientation distribution function. The ODF is defined in terms of the mesoscopic mass density (see eq. 1), and a differential equation for the distribution function can be derived from the mesoscopic balance of mass:

$$\begin{aligned} \frac{\partial}{\partial t}f(\cdot) \quad &+\quad \nabla_x \cdot [v(\cdot)f(\cdot)] + \nabla_n \cdot [u(\cdot)f(\cdot)] + \\ &+\quad f(\cdot)\left[\frac{\partial}{\partial t} + v(\cdot)\cdot\nabla_x\right] \ln\rho(x,t) \;=\; 0 \quad . \end{aligned} \tag{9}$$

The time evolution of the ODF depends essentially on the orientation change velocity u. Special cases are a reorientation of the preferred orientation (the rotation symmetry axis d) as it is caused by a flow field (see first example in Figure 5), or pure orientation diffusion, leading to a decrease of the orientational order (see second example in Figure 5), or an increase of the orientational order, caused for instance by an electric field (see third example in Figure 5).

An expression for the orientation change velocity has been derived from the balance of spin in Ehrentraut *et al.* (1997), Muschik *et al.* (1997), and Papenfuss (1998) under the following assumptions

(1) The mesoscopic material velocity does not depend on the orientation, that means it is equal to the barycentric velocity of the volume element.
(2) The liquid crystal is incompressible.
(3) There are no spatial gradients, except for a constant velocity gradient.
(4) There is no non-convective flux of spin on the mesoscopic level:

$$W(\cdot) = 0\,. \tag{10}$$

(5) The spin is stationary on relevant time scales.

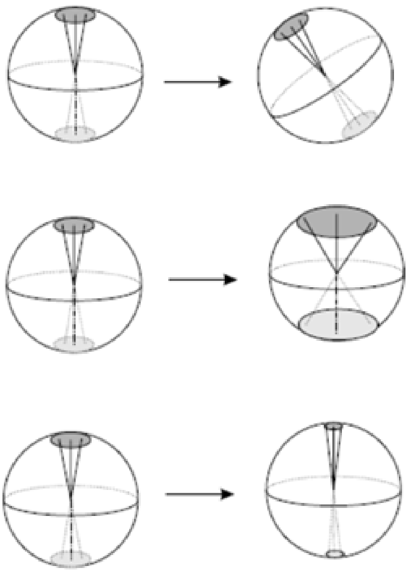


FIGURE 5. Different examples of the time evolution of the orientation distribution function.

These assumptions, together with a choice of the mesoscopic state space, lead to the expression for the orientation change velocity (Ehrentraut *et al.* 1997; Muschik *et al.* 1997):

$$u = \omega \times n + \beta_1 \frac{\nabla_n \rho(\cdot)}{\rho(\cdot)} + (\delta - nn) \cdot \Big(\beta_2 \, \overline{\nabla_x v} \, + \beta_3 a\Big) \cdot n \, . \tag{11}$$

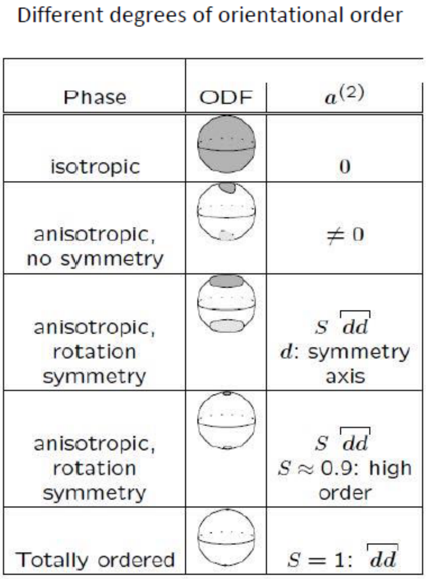
a is the second order alignment tensor, introduced in the next section. ω is the vorticity of the flow field, and δ is the unit tensor. β_1, β_2, and β_3 are material parameters. The first term accounts for the influence of orientation diffusion, the second one is the influence of the flow field, and the last one the orienting influence of the surrounding particles.

Inserting this expression (11) into the differential equation for the ODF, we end up with a differential equation of Fokker-Planck type for the orientation distribution function (Muschik and Su 1991):

$$\begin{aligned} \frac{d}{dt} f + \beta_1 \nabla_n \cdot \nabla_n f - 3 f n \cdot \{\beta_2 \, \overline{\nabla_x v} \, + \beta_3 a\} \cdot n \\ + \Big(\omega \times n + n \cdot \{\beta_2 \, \overline{\nabla_x v} \, + \beta_3 a\}\Big) \cdot \nabla_n f = 0 \end{aligned} \tag{12}$$

with the material time derivative

$$\frac{df}{dt} := \frac{\partial f}{\partial t} + v \cdot \nabla_x f \, . \tag{13}$$



Different degrees of orientational order

Phase	ODF	$a^{(2)}$
isotropic		0
anisotropic, no symmetry		$\neq 0$
anisotropic, rotation symmetry		$S\ \overline{dd}$ d: symmetry axis
anisotropic, rotation symmetry		$S\ \overline{dd}$ $S \approx 0.9$: high order
Totally ordered		$S = 1$: $\overline{dd}$

FIGURE 6. Different orientation distribution functions and corresponding alignment tensors.

2.4. Alignment tensors. The macroscopic parameters, describing the orientational order, are the alignment tensors. They are defined in terms of the ODF:

$$a(x,t) := a^{(2)}(x,t) = \int_{S^2} f(\cdot)\ \overline{nn}\ d^2n, \tag{14}$$

$$a^{(4)}(x,t) := \int_{S^2} f(\cdot)\ \overline{nnnn}\ d^2n, \tag{15}$$

$$a^{(6)}(x,t) := \int_{S^2} f(\cdot) \underbrace{\overline{n\dots n}}_{\text{6 times}} d^2n, \qquad \text{etc.} \tag{16}$$

$$a^{(k)}(x,t) := \int_{S^2} f(\cdot) \underbrace{\overline{n\dots n}}_{\text{k times}} d^2n\ . \tag{17}$$

These are tensors of successive order. Only the even order tensors are non-zero, due to the inversion symmetry of the orientation distribution function ($f(x,-n,t) = f(x,n,t)$). The symbol $\overline{}$ denotes the traceless symmetric part of the tensor in its argument (Blenk *et al.* 1991).

The alignment tensors are macroscopic quantities, but they contain information on the orientational order present on the mesoscopic level. The second order alignment tensor allows to classify the different types of orientational order (see figure 6).

The alignment tensors are internal variables in the sense of thermodynamics, and the second order alignment tensor is the order parameter in the Landau theory of the phase transition between the nematic liquid crystalline phase and the isotropic phase.

3. Dynamics of the alignment tensors on different levels of approximation

3.1. Dynamics of the second order alignment tensor. Multiplication of equation (12) by $\overline{nn}$, integration over the microscopic directors, and introducing the abbreviation for the non-traceless fourth moment of the ODF:

$$A^{(4)}(x,t) := \int_{S^2} f(n,x,t)nnnnd^2n \tag{18}$$

leads to the following differential equation for the second order alignment tensor:

$$\begin{aligned}\frac{d}{dt}a - 2\,\overline{\omega \times a} = {} & 6\beta_1 a + \frac{2}{5}\left(\beta_2\,\overline{\nabla_x v} + \beta_3 a\right)\\ & + \frac{6}{7}\,\overline{\left(\beta_2\,\overline{\nabla v} + \beta_3 a\right)\cdot a} - 2\,\overline{a : A^{(4)}}\ .\end{aligned} \tag{19}$$

The derivation can be found in Ehrentraut *et al.* (1997) and Muschik *et al.* (1997). The left hand side is the co-rotational time derivative of the second order alignment tensor.

This is not yet a closed differential equation for the second order alignment tensor, but a closure relation for the fourth moment $A^{(4)}$ is needed. One possibility is an algebraic relation between the fourth moment and the second order alignment tensor, for example

$$\begin{aligned}A^{(4)} = \int_{S^2} f(\cdot)nnnnd^2n &= \int_{S^2} f(\cdot)nnd^2n \int_{S^2} f(\cdot)nnd^2n\\ &= \left(a + \frac{1}{3}\delta\right)\left(a + \frac{1}{3}\delta\right)\end{aligned} \tag{20}$$

A more sophisticated possibility is to derive a closure relation from a maximization of entropy (Papenfuss and Muschik 1999), but this will not be discussed here.

With the closure relation (20), equation (19) leads to

$$\begin{aligned}\frac{d}{dt}a - 2\,\overline{\omega \times a} = {} & 6\beta_1 a + \frac{2}{5}\left(\beta_2\,\overline{\nabla_x v} + \beta_3 a\right)\\ & + \frac{6}{7}\,\overline{\left(\beta_2\,\overline{\nabla_x v} + \beta_3 a\right)\cdot a} - 2a : aa\end{aligned} \tag{21}$$

3.2. The uniaxial case. In most experimental situations a uniaxial symmetry of liquid crystals is observed with one distinguished axis d. This corresponds to an ODF, which is rotation symmetric with axis of rotation symmetry d. Then, for symmetry reasons the alignment tensors can be written as:

$$a^{(k)} = S^{(k)}\,\underbrace{\overline{d\ldots\ldots d}}_{\text{k times}} \tag{22}$$

with scalar order parameters $S^{(k)}$, and a unit vector d.

3.3. Landau theory of liquid crystals as a special case. For vanishing velocity field:

$$v \equiv 0 \rightarrow \nabla_x v \equiv 0 \tag{23}$$

the differential equation for the alignment tensor simplifies to:

$$\frac{d}{dt}a = 6\beta_1 a + \frac{2}{5}\beta_3 a + \frac{6}{7}\,\overline{\beta_3 a \cdot a} - 2a : aa = \overline{\frac{d\Sigma}{da}}\ , \tag{24}$$

which shows that the dynamics of the alignment tensor is derived from a potential of the form

$$\Sigma = \frac{1}{2}A(T)a:a - \frac{1}{3}B\,\mathrm{trace}\,(a\cdot a\cdot a) + \frac{1}{4}C_1\,(a:a)^2 + C_2\,\mathrm{trace}\,(a\cdot a\cdot a\cdot a), \tag{25}$$

where the coefficients are identified as

$$\begin{aligned} A(T) &= 6\beta_1 + \frac{2}{5}\beta_3 \\ B &= \frac{6}{7}\beta_3 \\ C_1 &= -2 \\ C_2 &= 0. \end{aligned} \tag{26}$$

The right hand side of this equation is proportional to the derivative of a potential. In other words, for vanishing velocity field, the time derivative of the alignment tensor is governed by a potential. For a non-vanishing velocity gradient, such a derivation from a potential is possible only in very special flow geometries but not in general (See *et al.* 1990).

The equation of motion for the alignment tensor without a flow field (24) can be interpreted as the equation of motion for the order parameter in the dynamical Landau theory. Landau theory was developed to deal with phase transitions (Landau and Lifschitz 1984), originally with phase transitions in ferromagnetic materials. It has been applied to various kinds of phase transitions, for instance: the transition nematic/isotropic phase in liquid crystals (Longa *et al.* 1987; Vertogen and deJeu 1988; De Gennes 1992; Virga 1994; De Gennes and Prost 1995), other transitions between liquid crystalline phases (De Gennes 1974; Grebel *et al.* 1983, 1984), the transition to the superfluid phase of liquid helium, and the transition to the superconductive phase (Landau and Ginzburg 1950). In general, it is assumed that there exists an order parameter that is nonzero in one phase (usually the lower temperature phase) and zero in the other phase. The free energy density f is assumed to depend on this order parameter in an analytical way, and the series expansion of the free energy density, with respect to the order parameter, is truncated at some order. The equation of motion for the order parameter O is postulated to be of the form:

$$\frac{dO}{dt} = C\frac{df}{dO}, \tag{27}$$

(with a constant C) which leads to the equilibrium condition:

$$\frac{df}{dO} = 0, \tag{28}$$

the necessary condition for an extremum of the free energy.

The equation of motion for the alignment tensor (24) is of the form of equation (27). The corresponding equilibrium condition is:

$$\frac{\Sigma}{da} = 0\,. \tag{29}$$

Consequently

$$A(T)a - B\,\overline{a\cdot a}\, + C_1 a : aa + C_2\,\overline{a\cdot a\cdot a} = 0\,. \tag{30}$$

The number of extremum values of the free energy expression depends on the value of the coefficient $A(T)$, which changes with temperature. This will be discussed here for the case of a uniaxial phase (the experimentally most important case) with axis of rotation symmetry d. Then the products of the alignment tensor $a = S\,\overline{dd} = S\left(dd - \frac{1}{3}\delta\right)$ with $d\cdot d = 1$ can be calculated, and it follows from the equilibrium condition (29):

$$A(T)S\,\overline{dd}\, - \frac{1}{3}BS^2\,\overline{dd}\, + \frac{2}{3}C_1S^3\,\overline{dd}\, + \frac{1}{3}C_2S^3\,\overline{dd} = 0 \tag{31}$$

and consequently

$$A(T)S - \frac{1}{3}BS^2 + \frac{2}{3}C_1S^3 + \frac{1}{3}C_2S^3 = 0\,, \tag{32}$$

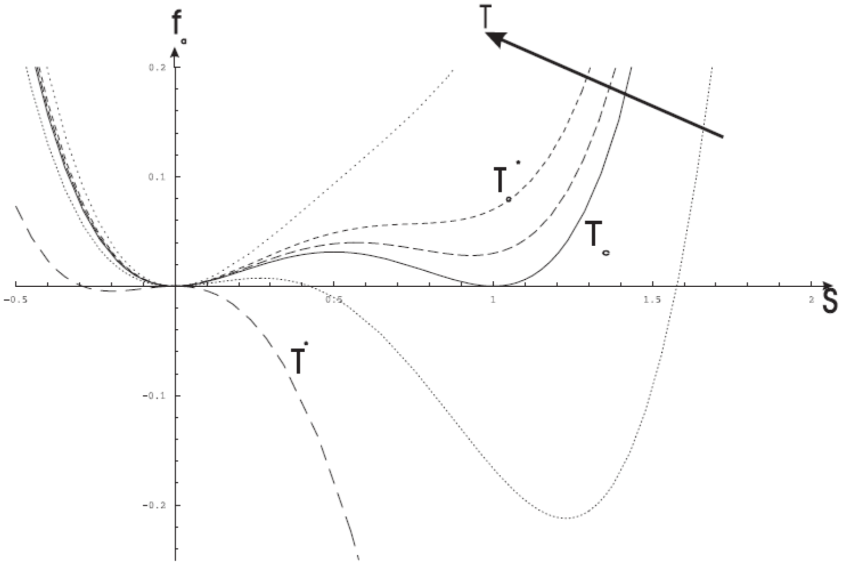


FIGURE 7. The free energy density as a function of the scalar order parameter for different temperatures.

At high temperatures T, there exists only one minimum of the free energy density at $S = 0$, the isotropic phase (see Figure 7). On lowering the temperature, there occurs a second minimum at temperature $T = T_c^*$, at which the value of the free energy is higher then at the isotropic minimum. This second minimum is meta-stable, and the corresponding ordered phase can be obtained as a meta-stable phase by overheating. At the temperature T_c, both minima have the same value of the free energy. At this temperature, the clearing temperature, there occurs the phase transition. The order parameter jumps between zero (isotropic phase) and a finite non-zero value (ordered phase). As the variable S is discontinuous at the phase transition, it is a first order transition. On lowering the temperature further, the second minimum becomes the absolute minimum and the liquid crystalline phase is the stable one. The isotropic phase (the minimum at order parameter zero) becomes unstable at temperature $T = T^*$. Up to this temperature, the isotropic phase can be obtained by supercooling as a meta-stable phase.

3.4. Dynamics of higher order alignment tensors. The second order alignment tensor does not contain the complete information on the orientation distribution function. The ODF can be reconstructed only from the whole infinite set of alignment tensors. And from equation (19) we see that, in the dynamics of the second order alignment tensor a, the fourth order alignment tensor $a^{(4)}$ plays a role. The alignment tensor theory may be refined by introducing the fourth order alignment tensor or even higher order tensors as additional independent variables. In this case, additional equations of motion for the higher order tensors are needed. In this section, we will present a derivation of these differential equations from the equation of motion for the ODF (12). This refinement of the alignment tensor theory has not been considered in the literature so far.

The alignment tensors have been defined as traceless tensors of successive order. For the sake of simplicity, we introduce in addition the non-traceless moments

$$A^{(k)}(x,t) = \int_{S^2} f(n,x,t) \underbrace{n \dots n}_{k} d^2 n \, . \tag{33}$$

In the following, we use the abbreviation

$$B = \beta_2 \, \overline{\nabla_x v} \, + \beta_3 a \, . \tag{34}$$

The differential equation for the ODF eq. (12) is multiplied with the k-th order tensor $\underbrace{n \dots n}_{\text{k times}}$ and integrated over the unit sphere, resulting in the following differential equation:

$$\begin{aligned} \frac{d}{dt} A^{(k)} - k\omega \times A^{(k)} = k\beta_1 \left((k+1) A^{(k)} - (k-1) \left(A^{(k-2)} \delta \right)^{sym} \right) + \\ + k \left(\left(B \cdot A^{(k)} \right)^{sym} - B : A^{(k+2)} \right) . \end{aligned} \tag{35}$$

The derivation is shown explicitly in the Appendix.

3.4.1. *Uniaxial case.* In the practically most important case of a rotation symmetric distribution function, the uniaxial case, all moments of different order are of the form:

$$A^{(k)} = S^{(k)} \underbrace{d \dots d}_{\text{k}} , \tag{36}$$

i.e. we have k scalar parameters $S^{(k)}$ and one unit vector d. The k-fold scalar product of equation (35) with the tensor $\underbrace{d \dots d}_{\text{k}}$ leads to a differential equation for the scalar parameter $S^{(k)}$. Here, it is used the fact, that $d \cdot \dot{d} = 0$, because d is a unit vector, $d \cdot d = 1$. For the scalar parameter we find:

$$\dot{S}^{(k)} = k\beta_1 \left((k+1) S^{(k)} - (k-1) S^{(k-2)} \right) + k \left(B : dd S^{(k)} - B : dd S^{(k+2)} \right) . \tag{37}$$

These are differential equations for the scalar order parameters of different order $S^{(k)}$. Together with the macroscopic director d they determine the alignment tensors. The differential equation for the macroscopic director can also be derived from equation (35), by taking the $(k-1)$- fold scalar product with the tensor $\underbrace{d\ldots d}_{k-1}$:

$$\begin{aligned} \dot{d} - \omega \times d &= -4\beta_1 d + (\delta - dd)\cdot B \cdot d \\ &= -4\beta_1 d + (\delta - dd)\cdot \left(\beta_2 \; \overline{\nabla_x v} \; + \beta_3 a\right) \cdot d. \end{aligned} \tag{38}$$

The macroscopic director is reoriented by the flow field $\overline{\nabla_x v}$ and by the mean field of the surrounding oriented particles a.

The higher order parameter $S^{(k+2)}$ can be eliminated from the equation, but then, a closure relation for $S^{(k+4)}$ is needed. In order to eliminate $S^{(k+2)}$, equation (37) is solved for $S^{(k+2)}$:

$$S^{(k+2)} = \left(-\dot{S}^{(k)} + k\beta_1 \left((k+1)S^{(k)} - (k-1)S^{(k-2)}\right) + kB : ddS^{(k)}\right) \frac{1}{kB : dd}. \tag{39}$$

Analogously to equation (37) we obtain for the order parameter of order $k+2$:

$$\begin{aligned} \dot{S}^{(k+2)} = (k+2)\beta_1 &\left((k+3)S^{(k+2)} - (k+1)S^{(k)}\right) + \\ &(k+2)\left(B : ddS^{(k+2)} - B : ddS^{(k+4)}\right). \end{aligned} \tag{40}$$

$S^{(k+2)}$ can be eliminated by differentiating equation (37):

$$\begin{aligned} \ddot{S}^{(k)} = k\beta_1 &\left((k+1)\dot{S}^{(k)} - (k-1)\dot{S}^{(k-2)}\right) + k\left(\dot{B} : ddS^{(k)} + 2B : \dot{d}dS^{(k)}\right. \\ &\left. + B : dd\dot{S}^{(k)} - \dot{B} : ddS^{(k+2)} - 2B : \dot{d}dS^{(k+2)} - B : dd\dot{S}^{(k+2)}\right), \end{aligned} \tag{41}$$

and inserting equations (39) and (40).

Let us consider explicitly the case where the second and the fourth order alignment tensors are taken as independent variables, *i.e.* the case $k = 2$. In the uniaxial case, the macroscopic director d, the second order scalar parameter $S^{(2)}$ and the fourth order parameter $S^{(4)}$ are the independent variables. After eliminating the fourth order parameter, we end up with a second order differential equation for the second order parameter:

$$\begin{aligned} \ddot{S}^{(2)} = \dot{S}^{(2)} \left(26\beta_1 + 4B : dd\right) - \frac{\dot{B} : dd + 2B : \dot{d}d}{B : dd} \left(6\beta_1 S^{(2)} - \dot{S}^{(2)}\right) \\ - S^{(2)} \left(120\beta_1^2 + 40\beta_1 B : dd\right) - 8\left(B : dd\right)^2 \left(S^{(2)} - S^{(6)}\right) \end{aligned} \tag{42}$$

with

$$B = \beta_2 \; \overline{\nabla_x v} \; + \beta_3 a. \tag{43}$$

This differential equation is coupled with the equation of motion for the macroscopic director d, equation (38). A closure relation for the sixth moment $S^{(6)}$, which is not an independent variable, is needed in addition.

4. Concluding remarks

The alignment tensors, the internal variables of the complex material, have been introduced as moments of the orientation distribution function. The mesoscopic balance equations allow to derive a set of coupled differential equations for the alignment tensors. In the lowest order theory, only the second order alignment tensor is an independent variable, and the fourth order tensor is eliminated by an algebraic closure relation. At this level of approximation, the dynamical Landau theory of phase transitions could be recovered in the special case of a liquid crystal at rest. The parameters of the Landau theory can be expressed in terms of phase transition temperature and the temperatures up to which the nematic phase can be overheated or the isotropic phase can be undercooled, respectively. These temperatures are available by experiment. Therefore, the comparison with Landau theory allows to identify the mesoscopic material parameters β_1 and β_3.

From the differential equation for the orientation distribution function, equations of motion for the alignment tensors of any order can be derived. This infinite set of equations is coupled, and the reduction to a limited number of alignment tensors requires a closure relation. In the lowest order approximation, only the second order alignment tensor is an independent variable, and only one differential equation is considered. On the next level of approximation, the second and the fourth order alignment tensors are independent variables, and their differential equations are derived. Then the sixth order tensor has to be eliminated by an algebraic relation. However, often the second order alignment tensor is the only one available from experimental data, and the fourth order tensor must be eliminated from the final set of equations. We have treated this situation explicitly for a uniaxial orientation distribution function. The result is a differential equation for the second scalar order parameter being of second order in time. This example shows that the final set of equations for the relevant order parameters is not limited to first order equations in time. Although the differential equation for the distribution function is of first order in time, as well as the infinite hierarchy of differential equations for the moments, closing this set of equations and eliminating the fourth order moment from the equations, leads to a differential equation of second order in time for the second order moment. This second order time derivative can be understood as a correction term, appearing in the more refined description, taking also the fourth moment as an independent variable. It does not occur at the lowest level of accuracy, namely, taking only the differential equation for the second moment, see subsection **3.1** and Ehrentraut *et al.* (1997), Muschik *et al.* (1997), and Papenfuss (1998).

The mesoscopically derived equations for the order parameter can be even of higher than second order in time, if higher order tensors than the fourth order one are taken as independent variables and eliminated later. The order of the final differential equation depends on the level, at which the set of equations is closed.

Space derivatives of alignment tensors do not appear here in the equations, because we have restricted ourselves to uniform systems. However, gradients can be taken into account in the state space. With gradient dependent constitutive functions, such spatial inhomogeneities are introduced into the differential equation for the distribution function and into the equations for the alignment tensors, via the orientation change velocity u. For the simple case of considering the second order alignment tensor as the only variable, such a gradient dependence has been considered in Papenfuss (1998).

Appendix: Derivation of the differential equations for the alignment tensors

Multiplication of the differential equation for the ODF eq. (12) with the k-th order tensor $\underbrace{n\dots n}_{\text{k times}}$ and integration over the unit sphere leads to

$$
\begin{aligned}
\frac{d}{dt}A^{(k)} &= \frac{d}{dt}\int_{S^2} f\underbrace{n\dots n}_{k}d^2n \\
&= -\int_{S^2}\nabla_n\cdot(uf)\underbrace{n\dots n}_{k}d^2n \\
&= \int_{S^2} fu\cdot\nabla_n\left(\underbrace{n\dots n}_{k}\right)d^2n \\
&= k\int_{S^2} f\left(u\underbrace{n\dots n}_{k-1}\right)^{sym}d^2n \\
&= k\int_{S^2} f\left(\omega\times n\underbrace{n\dots n}_{k-1}\right)^{sym}d^2n + k\int_{S^2} f\left(\beta_1\frac{\nabla_n\rho(\cdot)}{\rho(\cdot)}\underbrace{n\dots n}_{k-1}\right)^{sym}d^2n+ \\
&\quad +k\int_{S^2} f\left(P\cdot B\cdot n\underbrace{n\dots n}_{k-1}\right)^{sym}d^2n \\
&= k\left(\omega\times\int_{S^2} fn\underbrace{n\dots n}_{k-1}d^2n\right)^{sym} + k\int_{S^2}\frac{\rho(\cdot)}{\rho(x,t)}\beta_1\left(P\cdot\frac{\nabla_n\rho(\cdot)}{\rho(\cdot)}\underbrace{n\dots n}_{k-1}\right)^{sym}d^2n+ \\
&\quad +k\int_{S^2} f\left(P\cdot B\cdot n\underbrace{n\dots n}_{k-1}\right)^{sym}d^2n \\
&= k\left(\omega\times A^{(k)}\right)^{sym} + k\beta_1\frac{1}{\rho(x,t)}\Bigg(\underbrace{\int_{S^2}\nabla_n\cdot\left(P\rho(\cdot)\underbrace{n\dots n}_{k-1}\right)d^2n}_{=0}+ \\
&\quad -\int_{S^2}\left((\nabla_n\cdot P)\rho(\cdot)\underbrace{n\dots n}_{k-1}\right)^{sym}d^2n - \int_{S^2}\left(\nabla_n\left(\underbrace{n\dots n}_{k-1}\right)\rho(\cdot)\right)^{sym}d^2n\Bigg)+ \\
&\quad +k\int_{S^2} f\left(P\cdot B\cdot n\underbrace{n\dots n}_{k-1}\right)^{sym}d^2n
\end{aligned}
$$

$$\begin{aligned}
&= k\left(\omega \times A^{(k)}\right)^{sym} + k\beta_1 \frac{1}{\rho(x,t)} \left(\int_{S^2} 2\rho(\cdot) \underbrace{n\ldots n}_{k} d^2n + \right. \\
&\quad - \int_{S^2} (k-1)\rho(\cdot) \left(\underbrace{n\ldots n}_{k-2} \delta \right)^{sym} d^2n + \left. \int_{S^2} \rho(\cdot)(k-1) \underbrace{n\ldots n}_{k} d^2n \right) + \\
&\quad + k \int_{S^2} f \left((\delta - nn)\cdot B \cdot n \underbrace{n\ldots n}_{k-1} \right)^{sym} d^2n \\
&= k\left(\omega \times A^{(k)}\right)^{sym} + k\beta_1 \left((k+1)A^{(k)} - (k-1)\left(A^{(k-2)}\delta\right)^{sym} \right) + \\
&\quad + k\left(\left(B\cdot A^{(k)}\right)^{sym} - B : A^{(k+2)} \right) ,
\end{aligned} \tag{44}$$

where $(\quad)^{symm}$ denotes the symmetric part of a tensor.

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