

Continuum Thermodynamics of Two Dimensional Liquid Crystals

CHRISTINA PAPENFUSS¹ AND WOLFGANG MUSCHIK²

*Institut für Theoretische Physik, Technische Universität Berlin
Hardenbergstr. 36, D-10623 Berlin, Germany*

e-mail: ¹cpap0433@w421rz.physik.tu-berlin.de, ²womu0433@w421rz.physik.tu-berlin.de

AMS Subject Class. (1991): 76A15

1. INTRODUCTION

Liquid crystals consist of formanisotropic molecules. We assume here that the molecules are rotationally symmetric. Liquid crystals are distinguished from isotropic liquids by the fact that they exhibit a long range orientational ordering. In contrast to crystals there is no (three dimensional) positional ordering of the centers of mass of molecules present in liquid crystals.

There are important experimental examples of liquid crystals, which can be considered as two dimensional (see figure 1): Over a hole in a metal plate a free standing liquid crystalline film can be produced, which is only a few molecular layers thick. Another example is the phase boundary between the nematic phase and the isotropic phase. Other examples are boundary layers at a glass surface or lyotropic double layers. These double layers are biologically important as cell-membranes. The aim of the present work is a continuum thermodynamical description of such two dimensional liquid crystals.

physical system	G^+	G^-	material flux through S
phase boundary	nematic	isotropic phase	$\neq 0$
lyotropic membrane	solution of in water	amphiphilic comp.	$\neq 0$
free standing film	air	air	0

Table 1: The physical meaning of the bulk regions for the different examples.

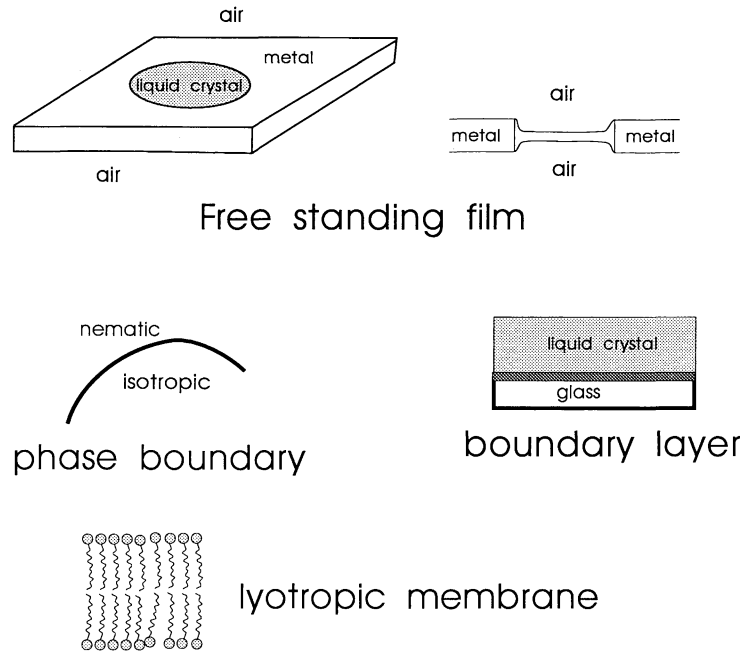


Figure 1: Free standing liquid crystalline films, phase boundaries and boundary layers are examples of two dimensional liquid crystals.

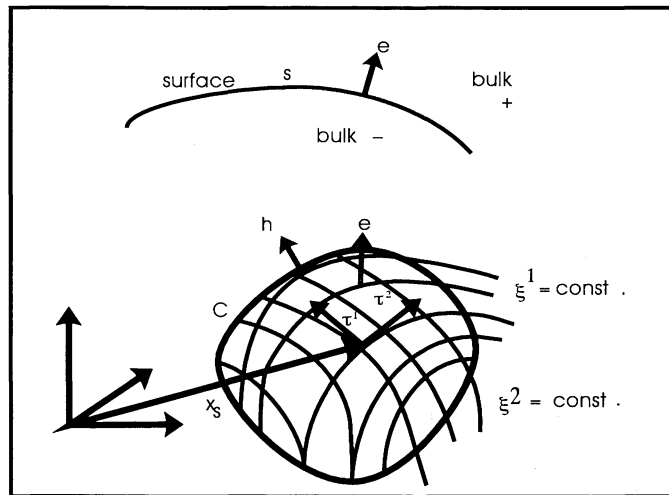


Figure 2: Geometry of the curved surface.

The liquid crystal is idealized as a surface, i. e. the thickness of a membrane, a free standing film and so on is not taken into account. The liquid crystal is a two dimensional submanifold, embedded in \mathbb{R}^3 . The surface divides the bulk into the regions + and -. The physical meaning of the bulk regions for the different examples is summarized in table 1. Gauss' basis of the tangential space to the surface is denoted with τ^1 and τ^2 , the unit normal vector (pointing towards the +-region) with \underline{e} (see figure 2).

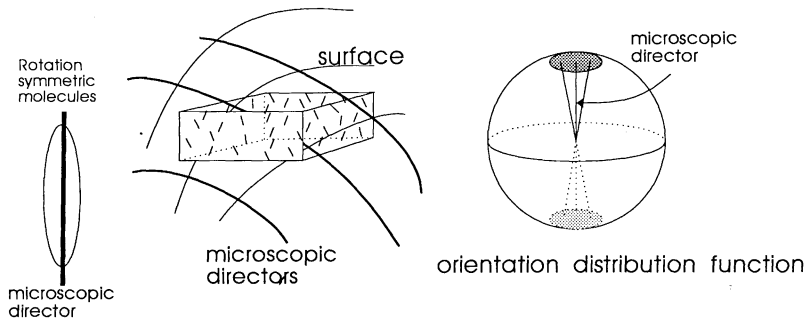


Figure 3: The orientational order of the uniaxial particles is described by an orientation distribution function.

1.1. DESCRIPTION OF THE LIQUID CRYSTALLINE ORDER: ALIGNMENT TENSORS. The liquid crystalline order is described by an orientation distribution function (ODF) $f(\underline{x}_s, \underline{n}, t)$

$$f: \mathfrak{N} \times \mathbb{R} \rightarrow \mathbb{R}^+ \quad ((\underline{x}_s, \underline{n}) \in \mathfrak{N}, t \in \mathbb{R}) \quad (1)$$

$$\int_{S^2} f(\underline{x}_s, \underline{n}, t) d^2 \underline{n} = 1 \quad (2)$$

$f(\underline{x}_s, \underline{n}, t)$ is the probability density of particles having orientation \underline{n} at position \underline{x}_s and time t . In the domain of the ODF \mathfrak{N} denotes the nematic space ($\mathfrak{S} \times S^2$) [3].

The ODF can be expanded with respect to a basis of Cartesian tensors [3], [2] $\overline{\underline{n} \dots \underline{n}}$, $\overline{\quad}$ denoting the symmetric traceless part of a tensor:

$$f(\underline{x}_s, \underline{n}, t) = \frac{1}{4\pi} \left(1 + \sum_{l=2, l \text{ even}}^{\infty} (2l-1)!! a_{m_1 \dots m_l}^{(l)}(\underline{x}_s, t) \overline{\underline{n}_{m_1} \dots \underline{n}_{m_l}} \right) . \quad (3)$$

The coefficients $a^{(l)}$ are called alignment tensors. They describe the liquid crystalline order.

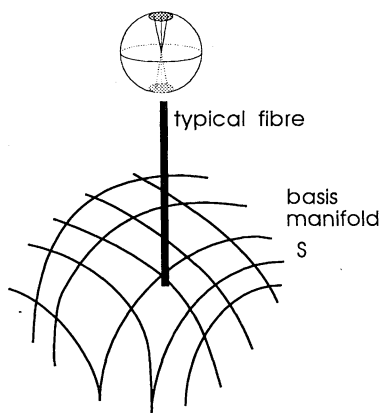


Figure 4: The nematic space. It can be formulated in terms of a fibre bundle.

2. DEFINITION OF SURFACE DENSITIES

Let ψ be a bulk density, for which we have an equation of motion

$$\frac{\partial \psi}{\partial t} = \check{F}[\psi] \quad (4)$$

with some functional $\check{F}[\psi]$. In the $+$ -region and in the $-$ -region of the bulk (see figure 2) we have

$$\frac{\partial \psi^\pm}{\partial t} = \check{F}[\psi^\pm], \quad (5)$$

i. e. ψ^+ and ψ^- are solutions of the differential equation (4), if no surface \mathcal{S} is present. Now we define fields $\tilde{\psi}_s$ as

$$\tilde{\psi}_s(\underline{r}, t) = \psi(\underline{r}, t) - \psi^-(\underline{r}, t)\Theta^-(\underline{r}, t) - \psi^+(\underline{r}, t)\Theta^+(\underline{r}, t) \quad (6)$$

$\psi(\underline{r}, t)$ is the field in the presence of the surface, whereas ψ^+ and ψ^- are the extrapolated bulk solutions. Θ^+ and Θ^- are the characteristic functions of the $+$ - and $-$ -region, respectively. The surface density ψ_s is the integral of the volume density $\tilde{\psi}_s$, integrated perpendicular to the surface over the surface region:

$$\psi_s = \int_{x_s-d}^{x_s+d} \tilde{\psi}_s ds. \quad (7)$$

The definition of the surface quantities is sketched in figure 5.

The physical surface densities are *defined* on the surface \mathfrak{S} , but the vectorial quantities are *not* elements of the tangential space $T_{x_s} \mathfrak{S}$. Their footpoint is an element of \mathfrak{S} , but they are elements of a three dimensional vector space. For example the velocity \underline{w} has a component normal to the surface \mathfrak{S} .

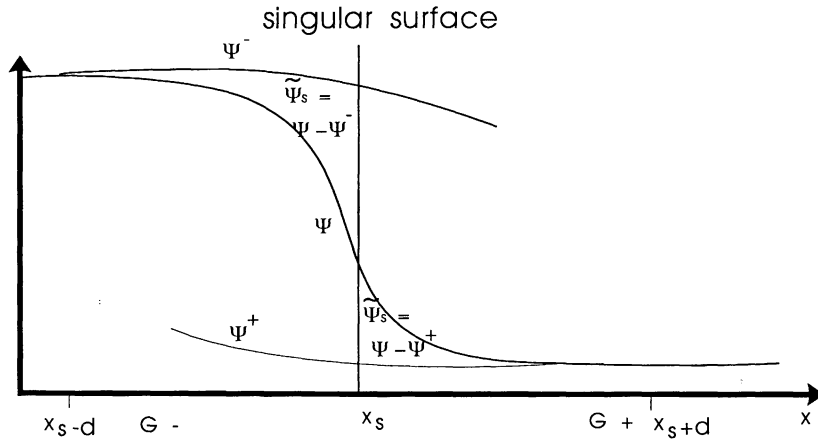


Figure 5: Definition of the surface fields: ψ^+ and ψ^- are the extrapolated bulk solutions, ψ is the solution in the presence of the surface (located at x_s). The difference between ψ^\pm and ψ , integrated over the surface region, defines the surface density ψ_s .

3. BALANCE EQUATIONS FOR SURFACE DENSITIES

The balance equation for an additive quantity Ψ_s within the time dependent subregion $G(t)$ of the surface is [1], [6], [7]:

$$\begin{aligned} \frac{d}{dt} \Psi_s &= \frac{\partial}{\partial t} \int_{G(t)} \psi_s(\xi^\alpha, t) da \\ &= - \int_{C(s)} \underline{\phi}_s \cdot \underline{h} ds - \int_{G(t)} \llbracket \underline{\phi} + \psi (\underline{v} - \underline{w}) \rrbracket \cdot \underline{e} da \\ &\quad + \int_{G(t)} (\pi_s + \sigma_s) da , \end{aligned} \tag{8}$$

ψ_s is the corresponding surface density (quantity per unit area), $\underline{\phi}_s$ is the flux through the boundary curve $C(s)$, π_s and σ_s are surface production and

supply density. \underline{h} is the outward unit normal vector to the curve $C(s)$ within the tangential plane to the surface \mathfrak{S} (see figure 2). $\underline{\phi}$ is the nonconvective bulk flux of the density ψ defined in the bulk. The brackets $\llbracket \]$ denote the difference between the limiting values ϕ_+ and ϕ_- of the bulk fields on both sides of the surface:

$$\llbracket \phi \rrbracket := \phi_+ - \phi_- . \quad (9)$$

The discontinuity of bulk fluxes contributes to the production of surface densities.

It is assumed that all surface densities are smoothly differentiable with respect to surface coordinates and with respect to time. Gauss' theorem is applied to the first expression on the left hand side.

A transport theorem has been derived [1] analogously to the derivation in \mathbb{R}^3 , mapping the surface regions to the reference configuration and taking into account the time dependence of the mapping and of the surface volume form. The result is

$$\frac{d}{dt} \int_{G(t)} \psi_s da = \int_{G(t)} \left(\frac{\partial \psi_s}{\partial t} + \nabla \cdot (\psi_s \underline{w}) - 2\psi_s K_M w^\perp \right) da . \quad (10)$$

\underline{w} is the mapping velocity, w^\perp is the component of \underline{w} normal to the surface and ∇ denotes the covariant derivative of the Levi-Civita-connection.

The third term on the right hand side of equation (10) arises from the time differentiation of the volume form in the actual configuration. As the resulting balance equation is valid for arbitrary surface regions we conclude the local form of the balance:

$$\frac{\partial \psi_s}{\partial t} - 2K_M w^\perp \psi_s + \nabla \cdot (\underline{\phi}_s + \psi_s \underline{w}) = -\llbracket \phi + \psi (\underline{v} - \underline{w}) \rrbracket \cdot \underline{e} + \pi_s + \sigma_s . \quad (11)$$

The balance equation (11) reduces to the Rankine-Hugoniot condition, if the surface is immaterial ($\rho_s = 0 \Rightarrow \psi_s = 0$) and there are no surface fluxes $\underline{\phi}_s$, productions π_s and supplies σ_s . Then the singular surface is a surface of discontinuity of the bulk quantities and the Rankine-Hugoniot jump conditions can be derived from the weak formulation of the balance equations in the bulk [5].

Now the quantities in the general balance equation (11) have to be identified with physical quantities. This is done in table 2 and in table 3.

balance of	ψ_s	$\underline{\phi}_s$	π_s	σ_s	ψ	$\underline{\phi}$
mass	ρ_s	0	0	0	ρ	0
momentum	$\rho_s \underline{w}$	$-\underline{t}_s$	0	$\rho_s \underline{f}_s$	$\rho \underline{v}$	$-\underline{t}$
angular momentum	$\rho_s (\underline{x}_s \times \underline{w} + \underline{s}_s)$	$-\underline{x}_s \times \underline{t}_s - \underline{\Pi}_s$	0	$\rho_s (\underline{x}_s \times \underline{f}_s + \underline{m}_s)$	$\rho (\underline{x} \times \underline{v} + \underline{s})$	$-\underline{x} \times \underline{t} - \underline{\Pi}$
energy	$\rho_s (e_s + 1/2 \underline{w} \cdot \underline{w} + \frac{1}{2\theta_{eff}} \underline{s}_s \cdot \underline{s}_s)$	$\underline{q}_s - \underline{w} \cdot \underline{t}_s - \frac{1}{\theta_{eff}} \underline{s}_s \cdot \underline{\Pi}_s$	0	$\rho_s (\underline{f}_s \cdot \underline{w} + \frac{1}{\theta_{eff}} \underline{s}_s \cdot \underline{m}_s)$	$\rho (e + 1/2 \underline{v} \cdot \underline{v} + \frac{1}{2\theta_{eff}} \underline{s} \cdot \underline{s})$	$\underline{q} - \underline{v} \cdot \underline{t} - \frac{1}{\theta_{eff}} \underline{s} \cdot \underline{\Pi}$

Table 2: Identification of the quantities in the abstract balance with physical quantities.

symbol	physical quantity
ρ_s	surface mass density
\underline{v}	material velocity in the bulk
\underline{t}_s	surface stress tensor
\underline{t}	stress tensor defined in the bulk
\underline{f}	acceleration due to external fields
\underline{s}_s	spin per unit mass defined on the surface
$\underline{\Pi}_s$	surface couple stress tensor
\underline{m}_s	surface couple forces
\underline{s}	spin density in the bulk
$\underline{\Pi}$	bulk couple stress tensor
e_s	surface specific internal energy
e	specific internal energy in the bulk
\underline{q}_s	surface heat flux
\underline{q}	bulk heat flux
θ_{eff}	effective moment of inertia of the particles

Table 3: List of symbols used in the balance equations.

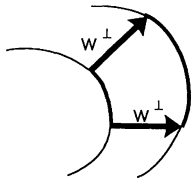

$$\begin{aligned}
\frac{\partial}{\partial t} \psi_s + \underbrace{\nabla \cdot (\psi_s \mathbf{w})}_{\text{convective flux within the surface}} + \underbrace{\nabla \cdot \underline{\phi}}_{\text{nonconvective flux}} \\
= \underbrace{-2\psi_s K_M w^\perp}_{\text{change of surface area}} \\
= \underbrace{\hat{\pi}_s}_{\text{production}} + \underbrace{\hat{\sigma}_s}_{\text{supply}} - \underbrace{\llbracket \underline{\phi} + \psi (\underline{v} - \underline{w}) \rrbracket \cdot \underline{e}}_{\text{discontinuity of bulk fluxes}}
\end{aligned}$$



Figure 6: Balance equation and interpretation of the terms.

Because of the internal structure of the medium (the needle shape of the particles) there exists an internal angular momentum (spin), and an antisymmetric part of the stress tensor, as well as couple stresses and couple forces acting on the particle orientation.

The velocity \underline{w} in the balance of momentum is *not* the material velocity, but the mapping velocity of the surface. For example in the case of a phase boundary the surface \mathfrak{S} is non-material. The balance of momentum determines the surface position and geometry at time t , having given the geometry in a reference configuration. Therefore the surface geometry at time t is not known a priori, but only after having solved the initial-(boundary-)value problem to the balance equations. This is similar to the situation in general relativity, where Einstein's equations for the metric tensor and the balance equations have to be solved simultaneously [8].

In addition to the mechanical balance equations a coupled system of differential equations for the alignment tensors of successive order has been derived [3]. We will consider only the second order alignment tensor \underline{a} as a wanted field. The mechanical balance equations are the equations of motion for the wanted fields of mass density ρ_s , momentum density $\rho_s \underline{w}$, spin density \underline{s}_s and internal energy density $\rho_s e_s$ with the domain of the fields being $\mathfrak{S} \times \mathbb{R}_t^+$. All other quantities in the balance equations are constitutive quantities. They depend on the thermodynamical state in a material dependent manner. The thermodynamical state is given by the fields $(\rho_s(\cdot), \underline{w}(\cdot), \underline{s}_s(\cdot), e_s(\cdot), \underline{a}_s(\cdot)) =: z_s(\cdot)$. In general constitutive quantities are functionals of the thermodynamic state. Here we will assume that constitutive quantities at position \underline{x}_s depend on the value of the state variables at \underline{x}_s and a limited number of gradients of $z_s(\cdot)$ at position \underline{x}_s . Constitutive quantities are then given by constitutive mappings defined on the (large) state space \mathfrak{Z} . This state space includes the state variables and the relevant gradients. A reasonable assumption of the variables being relevant to our problem is

$$\mathfrak{Z} = \{\rho_s, e_s, \nabla \rho_s, \nabla e_s, \underline{a}_s, \nabla \underline{a}_s, \nabla \nabla \underline{a}_s, \underline{s}_s, \nabla \underline{s}_s, \nabla \underline{w}, \underline{e}, \nabla \underline{e}, \underline{\tau}^1, \nabla \underline{\tau}^1, \underline{\tau}^2, \nabla \underline{\tau}^2\}. \quad (12)$$

Besides the state variables and their first spatial derivatives, the basis vectors of the tangential space $T_{\underline{x}_s} \mathfrak{S}$, the normal vector \underline{e} and their derivatives are included, i. e. constitutive quantities are allowed to depend on surface geometry. The partial space derivatives have been included and *not* the covariant derivatives. It is necessary to give up the requirement that all elements of the state space should transform like (surface-) tensors under changes of the surface coordinate system, because the surface geometry is not known a priori

and therefore covariant derivatives cannot be evaluated.

4. RESTRICTIONS ON CONSTITUTIVE FUNCTIONS FROM THE SECOND LAW OF THERMODYNAMICS

The constitutive mappings are restricted by the Second Law of Thermodynamics: After introducing the constitutive mappings into the balance equations it results a system of partial differential equations for the wanted fields. Any solution of the corresponding initial- (boundary-) value problem has to guarantee a non-negative entropy production. (For a derivation of this statement from a physically motivated axiom see "W. Muschik: An amendment to the Second Law of Thermodynamics" in this volume.) As a consequence there is an algebraic system of constraints on derivatives of constitutive functions [9], [10]. In the case of two dimensional liquid crystals these constraints can be summarized as follows:

- The surface free energy does not depend on the highest gradients included in the state space, but is not restricted besides.
- For the difference between the entropy flux and the heat flux over temperature one has

$$\frac{\partial \underline{\phi}_s}{\partial u_A} - \frac{1}{T_s} \frac{\partial \underline{q}_s}{\partial u_A} = - \frac{\partial f_s}{\partial \underline{s}_s} \cdot \frac{\partial \underline{\Pi}_s}{\partial u_A} - \underline{e} \cdot \frac{\partial \underline{\Pi}_s}{\partial u_A} \frac{\partial f_s}{\partial s_s^\perp}, \quad (13)$$

$$\text{for } u_A \in \{\nabla \rho_s, \nabla e_s, \nabla \underline{a}_s\}, \quad (14)$$

i. e. the difference between the two fluxes does not vanish if the derivatives of the couple stresses do not vanish and the free energy density depends on the spin density. This shows that in liquid crystals entropy transport is possible not only by heat transport, but also by transport of orientational order.

- The constitutive mapping of the surface stress tensor is determined by the Second Law. The normal stresses, i. e. the part of the surface stress tensor projected orthogonal and tangential to the surface $\underline{e} \cdot \underline{t}_s \cdot \underline{P}$ (\underline{P} : projector onto the tangential plane to \mathfrak{S}) do not vanish in contrast to simple liquids. They are given by a lengthy expression involving derivatives of the free energy density with respect to the alignment tensor and with respect to the surface metric tensor [4]. This means that a force applied tangential to a liquid crystalline film results in a stress component normal to the film.

ACKNOWLEDGEMENTS

Valuable discussions with Harald Ehrentraut are gratefully acknowledged. The work has been supported financially by Draloric Company (D-95100 Selb), the European Union (grant ERBCHRXCT920007) and the Sfb 335 "Anisotrope Fluide".

REFERENCES

- [1] ALTS, T. , HUTTER, K. , I: Surface balance laws and their interpretation in terms of three dimensional balance laws averaged over the phase change boundary layer, II: Thermodynamics, III: Thermostatistics and its consequences, IV: On thermostatic stability and well-posedness, *J. Non-Equilibrium Thermodyn.* **13** (1988), 221–301.
- [2] BLENK, S. , EHRENTRAUT, H. , MUSCHIK, W. , Orientation balances for liquid crystals and their representation by alignment tensors, *Mol. Cryst. Liq. Cryst.* **204** (1991), 133–141.
- [3] BLENK, S. , EHRENTRAUT, H. , MUSCHIK, W. , Statistical foundation of macroscopic balances for liquid crystals in alignment tensor formulation, *Physica A* **174** (1991), 119–138.
- [4] MUSCHIK, W. , PAPENFUSS, C. , Constitutive theory for two dimensional liquid crystals, *Mol. Cryst. Liq. Cryst.* **262** (1995), 473–484.
- [5] COURANT, R. , HILBERT, D. , "Methods of Mathematical Physics", Vol. II, Interscience Publishers, New York, London, 1962.
- [6] GRAUEL, A. , "Feldtheoretische Beschreibung von Grenzflächen", Springer Verlag, Berlin, New York, London, 1989.
- [7] GURTIN, M.E. , On thermodynamical laws for the motion of a phase interface, *J. Appl. Math. Phys. (ZAMP)* **42** (1991), 370–388.
- [8] HEEMEYER, H. , "Pseudoriemannsche Faserbündel und ihre Anwendung in der allgemeinrelativistischen Thermodynamik", Wissenschaft- und Technik Verlag, Berlin, 1995.
- [9] SHIH LIU, I. , Method of lagrange multipliers for exploitation of the entropy principle, *Arch. Rat. Mech. Anal.* **46** (1972), 131–148.
- [10] MUSCHIK, W. , ELLINGHAUS, R. , Zur Auswertung von Dissipationsungleichungen, *Z. angew. Math. Mech. (ZAMM)* **68** (1988), 232–233.