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# Evolution criterion in nonequilibrium and a variational principle for equilibrium states of free-standing liquid crystalline films

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Starting out with the thermodynamic balance equations of liquid crystalline films and the second law of thermodynamics, an analog to the global surface free energy is derived whose time derivative is negative definite out of equilibrium and zero in equilibrium. This evolution criterion allows one to formulate a variational principle for the equilibrium states by minimizing the modified global surface free energy derived above. Thus the quantity which is extremal in equilibrium in the case of free-standing crystalline films is not presupposed *ad hoc*, but derived from an evolution criterion based on the second law. [S1063-651X(97)14308-2]

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## I. INTRODUCTION

There are different approaches to a formulation of thermodynamics in terms of modified variational principles: In some cases special constitutive equations (linear force-flux relations or even nonlinear force-flux relations, always assuming Onsager symmetry relations) have been inserted into the balance equations, and these equations, valid for the special chosen material, have been derived from an extremum principle [1,2]. The balance equations without constitutive assumptions can be derived from a variational principle, if the number of wanted fields is doubled, with the shortcoming that there is no physical interpretation of the additional fields. For a review and a classification of various modified variational principles, see, for instance, [3,4].

Our aim here is to derive equilibrium conditions for free-standing films of liquid crystals from a variational principle. To this end we start out with the derivation of an evolution criterion from the second law of thermodynamics. Such a criterion for the evolution of nonequilibrium states in time is of the form

$$\frac{d}{dt}\int_{G(t)}\{\cdots\}dV\leqslant 0 \tag{1}$$

and is interesting in itself. Other evolution criteria have been formulated, for example, a principle of maximum entropy production [5]. This principle, however, cannot be derived by tools of nonequilibrium thermodynamics in general.

If an evolution criterion (1) is established, we obtain immediately a variational principle for equilibrium states,

$$\int_{G(t)}\{\cdots\}dV\rightarrow(\text{minimal in equilibrium}), \tag{2}$$

if some presuppositions are satisfied. Such a variational principle for equilibrium states of liquid crystals in three-dimensional configurations has been derived in [6], using exactly the same methods as applied in the present work.

There are important examples of liquid crystals which can be regarded as two dimensional: A free-standing liquid crystalline film consisting of a few molecular layers can be produced over a hole in a metal plate. Another two-dimensional system represents the phase boundary between the nematic and isotropic phases. Other two-dimensional examples are boundary layers on a glass surface or lyotropic double layers representing biologically important cell membranes.

The considered surface is in general not flat. It is moving in time, and the surface geometry is time dependent. The mapping velocity of the system in consideration is $\underline{w}$, and $w^{\perp}$ is its component normal to the surface. The surface unit normal vector is denoted by $\underline{e}$, $K_M$ is the mean curvature of the surface, and the index ";" denotes the covariant derivative of the Levi-Cività connection on the surface. Latin indices refer to a Cartesian coordinate system in $\mathbb{R}^3$ and greek indices refer to a curvilinear surface coordinate system. The surface is embedded in the surrounding bulk medium, and the bulk fluxes are in general discontinuous at the surface (see Fig. 1). The difference between the values of the bulk fields on both sides of the surface is denoted by

$$[\phi]:=\phi^{+}\phi^{-}. \tag{3}$$

The fact that phase boundaries and the other mentioned examples are not mathematical surfaces in reality, but have a finite thickness, will be ignored in the following.

The balance equations for surface densities have been derived in [7,8]. They are summarized here ($\varrho_s$ is the surface mass density, $\underline{v}$ is the material velocity in the bulk, $\underline{\underline{t}}_s$ is the surface stress tensor, $\underline{\underline{t}}$ is the bulk stress tensor, $\underline{f}$ is the acceleration due to external fields, $\underline{s}_s$ is the surface spin per unit mass, $\underline{\underline{\Pi}}_s$ is the surface couple stress tensor, $\underline{m}_s$ are the surface couple forces, $\underline{s}$ is the bulk spin density, $\underline{\underline{\Pi}}$ is the

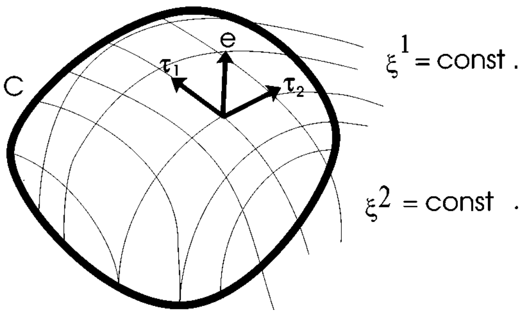

FIG. 1. Geometry of the curved surface.

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bulk couple stress tensor, $e_s$ is the surface specific internal energy, $e$ is the bulk specific internal energy, $\underline{q}_s$ is the surface heat flux, $\underline{q}$ is the bulk heat flux, and $\theta_{\mathrm{eff}}$ is the effective moment of inertia of the particles).

Balance of mass:

$$\frac{\partial}{\partial t}\,\varrho_s-2\varrho_s K_M w^{\perp}+(\varrho_s w^{\alpha})_{;\alpha}=-[\varrho(v^m-w^m)]e^m. \tag{4}$$

Balance of momentum:

$$\frac{\partial}{\partial t}\,(\varrho_s w^k)-2\varrho_s w^k K_M w^{\perp}+(\varrho_s w^k w^{\alpha}-t_s^{k\alpha})_{;\alpha}$$
$$=-[-t^{km}+\varrho v^k(v^m-w^m)]e^m+\varrho_s f^k. \tag{5}$$

Balance of internal angular momentum:

$$\frac{\partial}{\partial t}\,(\varrho_s s_s^k)-2K_M w^{\perp}\varrho_s s_s^k+(\varrho_s s_s^k w^{\alpha}-\Pi_s^{k\alpha})_{;\alpha}$$
$$=[\Pi^{km}-\varrho s^k(v^m-w^m)]e^m+\varrho_s m_s^k$$
$$+\epsilon^{klm}\tau_{\alpha}^{l}t_s^{m\alpha}+\epsilon_{\alpha\perp}^{k}\varrho_s w^{\perp}w^{\alpha}. \tag{6}$$

$\theta_{\mathrm{eff}}$ is an effective specific moment of inertia.

Balance of internal energy:

$$\frac{\partial}{\partial t}\,(e_s\varrho_s)-2K_M w^{\perp}\varrho_s e_s+q_{s;\alpha}^{\alpha}-w_{s;\alpha}^{k}t_s^{k\alpha}-\left(\frac{s_s^k}{\theta_{\mathrm{eff}}}\right)_{;\alpha}\Pi_s^{k\alpha}+(\varrho_s e_s w^{\alpha})_{;\alpha}$$
$$=-\left[q^m-(v^k-w^k)t^{km}+\left(\frac{1}{\theta_{\mathrm{eff}}}\,s^k-\frac{1}{\theta_{\mathrm{eff}}}\,s_s^k\right)\Pi^{km}+\varrho e(v^m-w^m)+\frac{\varrho}{2}\,(v^k-w^k)(v^k-w^k)\right.$$
$$\left.\times(v^m-w^m)+\frac{\varrho}{2\theta_{\mathrm{eff}}}\,(s^k-s_s^k)(s^k-s_s^k)(v^m-w^m)\right]e^m+\varrho_s r_s-\epsilon^{klm}\tau_{\alpha}^{l}t_s^{m\alpha}\,\frac{1}{\theta_{\mathrm{eff}}}\,s_s^k-\epsilon_{\alpha\perp}^{k}w^{\perp}w^{\alpha}\,\frac{1}{\theta_{\mathrm{eff}}}\,\varrho_s s_s^k. \tag{7}$$

In all these balance equations are terms which have no analog in the balance equations for three-dimensional liquid crystals: terms involving the mean curvature $K_M$ and terms due to discontinuities of the bulk fluxes. The first kind of terms are caused by the time rate of the moving surface area. The second kind of terms couple the surface balance equations to the balance equations in the bulk.

The local formulation of the second law of thermodynamics is the dissipation inequality on the surface ($\eta_s$) is the surface entropy density, $\underline{\phi}_s$ is the surface entropy flux, $\underline{\phi}$ is the entropy flux in the bulk, and $\sigma_s$ is the surface entropy production density):

$$\frac{\partial}{\partial t}\,(\varrho_s\eta_s)-2\varrho_s\eta_s K_M w^{\perp}+(\varrho_s\eta_s w^{\alpha}+\phi_s^{\alpha})_{;\alpha}$$
$$-[\varrho\,\eta(v^m-w^m)+\phi^m]e^m=\sigma_s\geqslant 0. \tag{8}$$

Liquid crystals in which we are interested here consist of form anisotropic molecules. As a result of this internal structure, there exists an internal angular momentum (spin). The orientational order of these anisotropic molecules is described by an orientation distribution function (ODF). The tensorial moments of this ODF are the alignment tensors $a^{(k)}$ of successive order [9], the second-order tensor is denoted with $\underline{\underline{a}}$.

## II. DERIVATION OF THE EVOLUTION CRITERION

Let us consider a liquid crystalline film in contact with a reservoir of given (constant) temperature $T^*$ and (constant) isotropic pressure $p^*$. The reservoir consists of a simple fluid, which means no couple stresses occur in the reservoir. For instance, for a free-standing liquid crystalline film the reservoir consists of the air surrounding the film from below and above, and of the metal plate surrounding the liquid crystal which is free standing over a hole in this metal plate (see Fig. 2). The liquid crystal brought into contact with the reservoir consists of the two bulk regions $G^+$ and $G^-$, which are separated by the surface $G$. The contacting surface between the liquid crystal and the reservoir is $\partial G$, consisting of (see Fig. 3)

$$\partial G=\partial G^+\cup\partial G^-\cup C. \tag{9}$$

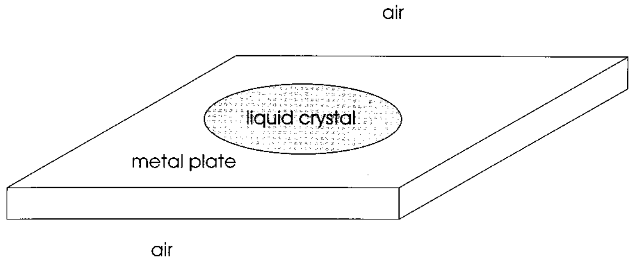

FIG. 2. Free-standing film over a hole in a metal plate.

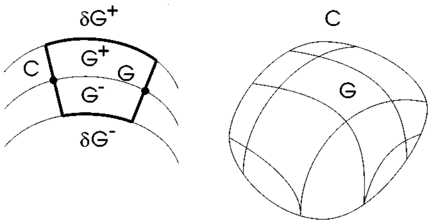

FIG. 3. The liquid crystal is in contact with a reservoir along the boundary $\partial G=\partial G^+\cup\partial G^-\cup C$.

Here $C$ is the cylindrical surface between the liquid crystal and metal plate. In the following it is assumed that the reservoir which is in contact with the liquid crystal is of uniform temperature $T^R$; i.e., the temperatures of the metal plate and of the surrounding air are presupposed to be equal.

On the contacting surface $\partial G^+ \cup \partial G^-$ (see Fig. 3), we have the same temperature and pressure as in the reservoir, and because of equilibrium between film and reservoir, the couple stresses vanish:

$$T_{\partial G^\pm} = T^R, \tag{10}$$

$$\Pi^{kl}_{\partial G^\pm} = 0, \tag{11}$$

$$\vartheta^l_{\partial G^\pm} := t^{lk}_{\partial G^\pm} n^k_{\partial G^\pm} = p^R n^l_{\partial G^\pm}. \tag{12}$$

On $C,$ we have

$$T_C = T^R, \tag{13}$$

$$\vartheta^\alpha_{sC} := t^{\alpha\beta}_{sC} h_\beta = p^R_C h^\alpha, \tag{14}$$

$$\Pi^{kl}_{sC} = 0. \tag{15}$$

The entropy flux through the surface in contact with the reservoir (which is in equilibrium per definition) is given by the heat flux over the temperature of the reservoir:

$$\underline{\phi}_s \Big|_C = \frac{1}{T^R}\, \underline{q}_s \Big| C \tag{16}$$

and

$$\underline{\phi} \Big|_{\partial G^\pm} = \frac{1}{T^R}\, \underline{q} \Big|_{\partial G^\pm}. \tag{17}$$

By Eq. (16), we obtain on the cylindrical surface $C$:

$$\int_C \phi^\alpha_s h_\alpha da = \frac{1}{T^R} \int_C q^\alpha_s h_\alpha da \tag{18}$$

and, analogously by Eq. (17) on the boundaries $\partial G^+$ or $\partial G^-$, respectively,

$$\int_{\partial G^\pm} \phi^{\pm k} e^k da = \frac{1}{T^R} \int_{\partial G^\pm} q^{\pm k} e^k da. \tag{19}$$

Now let the thickness of the regions $G^+$ and $G^-$ normal to the surface become infinitesimally small, and the cylindrical surface $C$ becomes the curve $C(s)$. Then the difference between both the integrals in Eq. (19) results in the surface integral over a jump contribution:

$$\int_{\partial G^+} \phi^{+k} e^k da - \int_{\partial G^-} \phi^{-k} e^k da \rightarrow \int_{G(t)} [\phi^k] e^k da, \tag{20}$$

$$\frac{1}{T^R} \int_{\partial G^+} q^{+k} e^k da - \frac{1}{T^R} \int_{\partial G^-} q^{-k} e^k da \rightarrow \frac{1}{T^R} \int_{G(t)} [q^k] e^k da, \tag{21}$$

and therefore we obtain in this limit

$$\int_{G(t)} [\phi^k] e^k da = \frac{1}{T^R} \int_{G(t)} [q^k] e^k da. \tag{22}$$

Because the film may absorb heat, $[q] \cdot \underline{e}$ is nonzero in general.

In contrast to the uniform temperature $T^R$ of the reservoirs, the stress tensors are differently defined on $\partial G^\pm$ and along $C(s)$:

$$p^R \neq p|^R_{C(s)}. \tag{23}$$

Even the units of $p^R$ and $p|^R_{C(s)}$, which are $\mathrm{N\,m^{-2}}$ and $\mathrm{N\,m^{-1}}$, are different.

Now Eqs. (18) and (22) are inserted into the global dissipation inequality:

$$\begin{aligned}
&\frac{d}{dt} \int_{G(t)} (\varrho_s \eta_s) da + \int_C \phi^\alpha h_\alpha ds - \int_{G(t)} [\phi^k + \varrho\, \eta (v^k - w^k)] e^k da \\
&= \frac{d}{dt} \int_{G(t)} (\varrho_s \eta_s) da + \int_C \frac{q^\alpha_s}{T^R} h_\alpha ds - \int_{G(t)} \left[ \frac{q^k}{T^R} + \varrho\, \eta (v^k - w^k) \right] e^k da \\
&= \frac{d}{dt} \int_{G(t)} (\varrho_s \eta_s) da + \int_{G(t)} \frac{q^\alpha_{s;\alpha}}{T^R} da - \int_{G(t)} \left[ \frac{q^k}{T^R} + \varrho\, \eta (v^k - w^k) \right] e^k da \geqslant 0.
\end{aligned} \tag{24}$$

To obtain an evolution criterion, we have to recase Eq. (24) in the form of time derivatives according to Eq. (1). Therefore the heat flux is substituted by the balance of internal energy (7):

$$\begin{aligned}\frac{d}{dt}\int_{G(t)}\varrho_s\eta_s da \geqslant{}& \int_{G(t)}[\varrho\,\eta(v^k-w^k)]e^k da+\frac{1}{T^R}\int_{G(t)}\Biggl\{-w^k_{;\alpha}t^{k\alpha}_s-\left(\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s\right)_{;\alpha}\Pi^{k\alpha}_s-\Biggl[(w^k-v^k)t^{km}\\ &+\left(\frac{1}{\theta_{\mathrm{eff}}}\,s^k-\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s\right)\Pi^{km}+\varrho e(v^m-w^m)\,\frac{\varrho}{2}\,(v^k-w^k)(v^k-w^k)(v^m-w^m)\\ &+\frac{\varrho}{2\,\theta_{\mathrm{eff}}}\,(s^k-s^k_s)(s^k-s^k_s)(v^m-w^m)\Biggr]e^m+\varrho_s r_s-\epsilon^{klm}\tau^l_\alpha t^{m\alpha}_s\,\frac{\varrho_s}{\theta_{\mathrm{eff}}}\,s^k_s\\ &-\epsilon^k_{\alpha\perp}w^\perp w^\alpha\,\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s da\Biggr\}da+\frac{1}{T^R}\,\frac{d}{dt}\int_{G(t)}\varrho_s e_s da. \end{aligned}\tag{25}$$

Define

$$I:=\int_{G(t)}\left[w^k_{;\alpha}t^{k\alpha}_s+\left(\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s\right)_{;\alpha}\Pi^{k\alpha}_s\right]da=\int_{C(s)}\left(w^k t^{k\alpha}_s+\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s\Pi^{k\alpha}_s\right)h_\alpha ds-\int_{G(t)}\left(w^k t^{k\alpha}_{s;\alpha}+\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s\Pi^{k\alpha}_{s;\alpha}\right)da. \tag{26}$$

The first term simplifies with the equilibrium conditions on the contacting surface:

$$l^{\alpha\beta}_{C(s)}h_\beta=p^R_s h^\alpha,\quad \Pi^{\alpha\beta}_{C(s)}=0,\quad t^{\perp\alpha}_{C(s)}=0, \tag{27}$$

$$I=p^R_s\int_{C(s)}w^\beta h_\beta ds-\int_{G(t)}\left(w^k t^{k\alpha}_{s;\alpha}+\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s\Pi^{k\alpha}_{s;\alpha}\right)da. \tag{28}$$

The integral $I$ simplifies using the surface transport theorem [7,8,10] for any surface density $\psi_s$:

$$\frac{d}{dt}\int_{G(t)}\psi_s da=\int_{G(t)}\left(\frac{\partial\psi_s}{\partial t}+(\psi_s w^\alpha)_{;\alpha}-2\,\psi_s K_M w^\perp\right)da, \tag{29}$$

with $\psi_s\equiv 1$,

$$I=p^R_s\left(\frac{d}{dt}\int_{G(t)}1da+\int_{G(t)}2w^\perp K_M da\right)-\int_{G(t)}\left(w^k t^{k\alpha}_{s;\alpha}+\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s\Pi^{k\alpha}_{s;\alpha}\right)da. \tag{30}$$

For the stress tensor the balance of momentum and for the couple stresses the spin balance are inserted:

$$\begin{aligned}I={}&p^R_s\left(\frac{d}{dt}\int_{G(t)}1da+\int_{G(t)}2w^\perp K_M da\right)-\int_{G(t)}w^k\{[-t^{km}+\varrho v^k(v^m-w^m)]e^m+\varrho_s f^k\}da-\frac{d}{dt}\int_{G(t)}\frac{1}{2}\,\varrho_s w^k w^k da\\ &+\frac{1}{2}\int_{G(t)}[\varrho(v^m-w^m)]e^m w^k w^k-\int_{G(t)}\left(\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s[\Pi^{km}-\varrho s^k(v^m-w^m)]e^m+\varrho_s m^k_s+\epsilon^{klm}\tau^l_\alpha t^{m\alpha}_s+\epsilon^k{}_{\alpha\perp}\varrho_s w^\perp w^\alpha\right)da\\ &-\frac{d}{dt}\int_{G(t)}\left(\frac{1}{2\,\theta_{\mathrm{eff}}}\,\varrho_s s^k_s s^k_s+\frac{1}{2}\,[\varrho(v^m-w^m)]e^m\,\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s s^k_s\right)da. \end{aligned}\tag{31}$$

Using these equations in the dissipation inequality, we obtain

$$\begin{aligned}\frac{d}{dt}\int_{G(t)}\varrho_s\eta_s da\geqslant{}&\int_{G(t)}\frac{1}{T^R}\,[\varrho\,\eta(v^k-w^k)]e^k da+\int_{G(t)}\Biggl(\Biggl[(v^k-w^k)t^{km}+\varrho e(v^m-w^m)+\frac{\varrho}{2}\,(v^k-w^k)(v^k-w^k)(v^m-w^m)\\ &+\frac{\varrho}{2\,\theta_{\mathrm{eff}}}\,(s^k-s^k_s)(s^k-s^k_s)(v^m-w^m)\Biggr]e^m+\varrho_s r_s-\epsilon^{klm}\tau^l_\alpha t^{m\alpha}_s\,\frac{\varrho_s}{\theta_{\mathrm{eff}}}\,s^k_s+\epsilon^k_{\alpha\perp}w^\perp w^\alpha\,\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s\Biggr)da\\ &+\frac{d}{dt}\int_{G(t)}\varrho_s e_s da-p^R_s\left(\frac{d}{dt}\int_{G(t)}1da+\int_{G(t)}2w^\perp K_M da\right)-\int_{G(t)}w^k\bigl([-t^{km}+\varrho v^k(v^m-w^m)]e^m\\ &+\varrho_s f^k\bigr)da+\int_{G(t)}\frac{1}{2}\,\varrho_s w^k w^k da-\int_{G(t)}(s^k_s[\Pi^{km}-\varrho s^k(v^m-w^m)]e^m+\varrho_s m^k_s+\epsilon^{klm}\tau^l_\alpha t^{m\alpha}_s\\ &+\epsilon^k_{\alpha\perp}\varrho_s w^\perp w^\alpha)da-\frac{d}{dt}\int_{G(t)}\left(\frac{1}{2\,\theta_{\mathrm{eff}}}\,\varrho_s s^k_s s^k_s+\frac{1}{2}\,[\varrho(v^m-w^m)]e^m\,\frac{1}{\theta_{\mathrm{eff}}}\,s^k_s s^k_s\right)da. \end{aligned}\tag{32}$$

We now assume that the film is at rest,

$$w^{\perp}=0, \tag{33}$$

and that there is no material flux through the film:

$$(v^m-w^m)e^m=0. \tag{34}$$

In addition we assume the external forces $\underline{f}$ to be conservative ($\underline{f}=-\underline{\nabla}\gamma_s$):

$$\begin{aligned}-\int_{G(t)}\varrho_s f^k w^k da&=\int_{G(t)}\varrho_s(\nabla^k\gamma_s)w^k da\\&=\int_{G(t)}\varrho_s[(\nabla_\alpha\gamma_s)w^\alpha+(\nabla_\perp\gamma_s)w^\perp]da\\&=\int_{G(t)}\varrho_s[\gamma_{s;\alpha}w^\alpha+(\nabla_\perp\gamma_s)w^\perp]da\\&=\frac{d}{dt}\int_{G(t)}\varrho_s\gamma_s da.\end{aligned} \tag{35}$$

Here Eq. (33) and the mass balance was inserted.

Finally from Eq. (32) by use of Eqs. (33) and (34), and multiplication by $-1$, we have obtained the evolution criterion we looked for:

$$\frac{d}{dt}\int_{G(t)}\left(-T^R\varrho_s\eta_s+\varrho_s e_s+p_s^R+\frac{1}{2}\varrho_s\underline{w}\cdot\underline{w}+\frac{\varrho_s}{2\theta_{\text{eff}}}\underline{s}_s\cdot\underline{s}_s+\varrho_s\gamma_s\right)da\leqslant 0\quad\forall t. \tag{36}$$

We now transform this evolution criterion into a more convienient form. The (global) kinetic energy $\int_{G(t)}(\varrho_s/2)\underline{w}\cdot\underline{w}da$ can be split into a sum of translational energy of the whole surface $G(t)$ and some contribution to the global internal energy:

$$\begin{aligned}\int_{G(t)}\frac{\varrho_s}{2}\underline{w}\cdot\underline{w}da&=\frac{1}{2}\underline{W}\cdot\underline{W}\int_{G(t)}\varrho_s da+\int_{G(t)}\frac{\varrho_s}{2}(\underline{w}-\underline{W})\cdot(\underline{w}-\underline{W})da\\&=\frac{M}{2}\underline{W}\cdot\underline{W}+\int_{G(t)}\varrho_s e_s' da,\end{aligned} \tag{37}$$

where $e_s'$ is the contribution to the internal energy of $G(t)$ and $\underline{W}$ is defined by use of the mean value theorem

$$M\underline{W}:=\int_{G(t)}\varrho_s\underline{w}\,da. \tag{38}$$

Similarly, by

$$M\underline{S}:=\int_{G(t)}\varrho_s\underline{s}_s da, \tag{39}$$

we obtain, for the spin density,

$$\int_{G(t)}\frac{\varrho_s}{2\theta_{\text{eff}}}\underline{s}_s\cdot\underline{s}_s da=\frac{M}{2\theta_{\text{eff}}}\underline{S}\cdot\underline{S}+\int_{G(t)}\frac{\varrho_s}{2\theta_{\text{eff}}}\times(\underline{s}_s-\underline{S})\cdot(\underline{s}_s-\underline{S})da. \tag{40}$$

Here the last term is another contribution to the global internal energy:

$$\int_{G(t)}\frac{\varrho_s}{2\theta_{\text{eff}}}(\underline{s}_s-\underline{S})\cdot(\underline{s}_s-\underline{S})da=:\int_{G(t)}\varrho_s e_s'' da. \tag{41}$$

For an observer moving with velocity $\underline{W}$ and angular velocity $(1/\theta_{\text{eff}})\underline{S}$, the first terms in Eqs. (37) and (40) vanish. With the definition

$$\overline{e_s}=e_s+e_s'+e_s'', \tag{42}$$

the integral (36) reads, for such an observer,

$$\begin{aligned}&\frac{d}{dt}\int_{G(t)}(-T^R\varrho_s\eta_s+\varrho_s\overline{e_s}+p_s^R+\gamma_s)da\\&=:\frac{d}{dt}\int_{G(t)}g\,da\leqslant 0\quad\forall t.\end{aligned} \tag{43}$$

Because the time derivative is strictly negative in nonequilibrium and zero in equilibrium, it follows that the integral is minimal at equilibrium. Consequently a variational principle can be formulated, which will be done in the next section. It has to be noted that the integrand does not depend explicitly on the mean curvature of the two-dimensional liquid crystal. As a consequence, the curvature does not occur in the resulting Euler-Lagrange equations explicitly (see the end of next section). This is also true for the electromagnetic fields. They enter only by the constitutive equations for the internal energy density and for the entropy density. Constitutive equations will not be discussed here further. An earlier publication [11] deals with implications of the second law on constitutive equations for two-dimensional liquid crystals.

## III. VARIATIONAL PRINCIPLE

Here we want to show that the evolution criterion derived in the previous section implies a variational principle for equilibrium states. To this end we assume that the following presupposition holds true.

The independent fields

$$\varrho_s, e_s, \underline{s}_s, \underline{w}_s, \underline{\underline{q}}_s \tag{44}$$

relax for sufficiently long time $\underline{t}$ to unique equilibrium values,

$$\begin{aligned}&\varrho_s|_{\text{eq}}(T^R,p_s^R), e_s|_{\text{eq}}(T^R,p_s^R), \underline{s}_s|_{\text{eq}}(T^R,p_s^R),\\&\underline{w}|_{\text{eq}}(T^R,p_s^R), \underline{\underline{q}}_s|_{\text{eq}}(T^R,p_s^R),\end{aligned} \tag{45}$$

which are determined by the equilibrium values $p_s^R$ and $T_s^R$ kept fixed during the relaxation by the controling reservoir. This equilibrium state is uniquely determined by the initial conditions and the environmental control (there is no branching during the process).

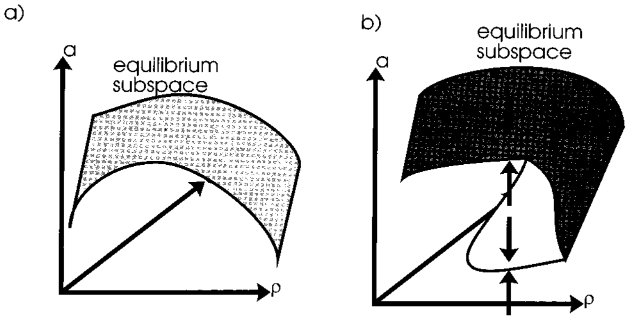

FIG. 4. The state space is spanned in this example by the density $\varrho$, the internal energy $e$, and the alignment tensor $\underline{\underline{a}}$. (a) The equilibrium subspace is a two-dimensional hypersurface in this state space. (b) The structure of the equilibrium subspace is such that for some values of $\varrho$ and $e$ there are two equilibrium values of $\underline{\underline{a}}$.

This uniqueness of the final equilibrium state must not be taken for the fact that in the case of possible phase transitions more than one value of

$$(\varrho_s|_{\rm eq}, e_s|_{\rm eq}, \underline{s}_s|_{\rm eq}, \underline{w}|_{\rm eq}, \underline{\underline{a}}_s|_{\rm eq})$$

belonging to the same controling parameters $(T^R, p_s^R)$ is possible, but only one is realized [see Fig. 4(b)].

We are now interested in a method of finding these equilibrium fields spanning the equilibrium subspace.

*Proposition*: The evolution criterion derived in the last section logether with the presupposition above implies a variational principle for equilibrium states.

An arbitrary nonequilibrium state can be taken as initial condition for a thermodynamic process, relaxing to the equilibrium state. From the evolution criterion, we know that along this process the integral

$$G(t) = \int_{G(t)} g \, da = \int_{G(t)} (\varrho_s \overline{e_s} - \varrho_s T^R \eta_s + p_s^R + \varrho_s \gamma_s) da \tag{46}$$

decreases. Therefore it is minimal in equilibrium compared to all nonequilibrium states for arbitrary, but kept fixed controling parameters $(T^R, p_s^R)$. As a result of the fact that the equilibrium is presupposed to be unique for fixed controlling parameters, there are no fields (44) for which Eq. (46) is less than in equilibrium according to the evolution criterion. That means the equilibrium fields have to minimize Eq. (46). The value of this minimum depends on the values of the controling parameters $(T^R, p_s^R)$. Thus we obtain the *variational principle*

$$G(\varrho_s(\cdot), e_s(\cdot), \underline{s}_s(\cdot), \underline{w}_s(\cdot), \underline{\underline{a}}_s(\cdot); T^R, p_s^R) \rightarrow \text{minimal} \tag{47}$$

in equilibrium with respect to arbitrary, but constant controlling fields at the boundary $C$.

The Euler-Lagrange equations belonging to this variational principle represent the equilibrium conditions. To write them down explicitly, one has to chose the variables of which the integrand in Eq. (46) depends on; that means that the state space has to be fixed. A reasonable choice for the state space for liquid crystals is [9,11]

$$Z = \{\varrho_s, e_s, \nabla \varrho_s, \nabla e_s, \underline{\underline{a}}_s, \nabla \underline{\underline{a}}_s, \nabla\nabla \underline{\underline{a}}_s, \nabla \underline{w}, \underline{\underline{g}}, \underline{\underline{b}}\} \tag{48}$$

($\underline{\underline{g}}$ is the surface metric tensor and $\underline{\underline{b}}$ is the curvature tensor). This state space is different from the independent fields (44) because constitutive properties of liquid crystals depends on the gradients of these fields. The surface spin $\underline{s}_s$ is a constitutive equation, which therefore does not appear in the state space. Also, the velocity of the surface $\underline{w}_s$ is not included in the state space because constitutive properties do not depend on the relative velocity between observer and the system due to the principle of objectivity [12]. The geometrical parameters $\underline{\underline{g}}$ and $\underline{\underline{b}}$ are kept constant in the variation because the geometrical properties of the surface are given and not wanted.

With the choice of the state space (48), the free energy density $g$ in Eq. (46) generates the Euler-Lagrange equations for the equilibrium fields $\varrho_s|_{\rm eq}$, $e_s|_{\rm eq}$, and $\underline{\underline{a}}|_{\rm eq}$:

$$\frac{\partial g}{\partial e_s} - \overline{\nabla}_\alpha \frac{\partial g}{\partial e_{s,\alpha}} = 0, \tag{49}$$

$$\frac{\partial g}{\partial \varrho_s} - \overline{\nabla}_\alpha \frac{\partial g}{\partial \varrho_{s,\alpha}} = 0, \tag{50}$$

$$\frac{\partial g}{\partial a_s^{kl}} - \overline{\nabla}_\alpha \frac{\partial g}{\partial a_{s,\alpha}^{kl}} + \overline{\nabla}_\alpha \overline{\nabla}_\beta \frac{\partial g}{\partial a_{s,\alpha\beta}^{kl}} = 0. \tag{51}$$

Because the integral (43) is on a curved manifold, here the surface $\underline{s}$, the derivatives in the Euler-Lagrange equations are covariant ones $\overline{\nabla}$. Because this covariant derivative depends on surface geometry, the Euler-Lagrange equations depend implicitly on curvature. Additionally, also the constitutive function $g$ may depend on the geometrical parameters which we have included in the state space (48).

## IV. CONCLUSIONS

It has been proved that the free energy $G(t)$ in Eq. (46) is minimal in equilibrium. This free energy is generated by integrating the special surface free energy density

$$g = \varrho_s \overline{e_s} - T^R \varrho_s \eta_s + p_s^R + \varrho_s \gamma_s \tag{52}$$

according to Eq. (46). Such a statement is usually introduced as an *ad hoc assumption* in Landau theory [13]: A surface free energy like Eq. (52) is written down by guess. The assumption that the global free energy belonging to the guessed surface free energy is extremal results in Euler-Lagrange equations which are the basis of Landau's theory. Here this procedure is derived by proving the variational principle (47), which stems from the evolution criterion [6] whose background is the second law.

An analogous variational principle has been proved for three-dimensional liquid crystals [6]. But treating the anchoring problem of liquid crystals at a surface the free energy used by other authors [14] consists of bulk and surface contributions. Hence the surface contributions are invariants generated by the alignment tensor or by the macroscopic director and by the normal vector of the surface. The corresponding bulk contributions are elastic energies, i.e., scalar invariants involving gradients of the alignment tensor or the macroscopic director, respectively. Such a variational principle cannot be obtained in the frame of the theory of a singular surface, because the here used dissipation inequality is valid for the surface and for the bulk separately. This results in separate variational principles for the surface and for the bulk. The question, if a coupling between bulk and surface terms occurs in the variational principle, if the boundary is not treated as a singular surface, but as a surface region of finite thickness with great field gradients will be examined elsewhere. Another possibility would be to include the fields of the adjacent bulk regions into the state space of the surface quantities.

With the special ansatz for the curvature dependence of the surface free energy

$$f_s = \tfrac{1}{2} k_c (K_M - c_0)^2 - \overline{k_c} K_G \tag{53}$$

[$k_c$, $c_0$, and $\overline{k_c}$ are material-dependent parameters and $K_G$ is the Gauss' curvature, $K_G = \det(\underline{\underline{b}})$], the variational principle (46) is the same used in [15,16] for lyotropic membranes. Note again that the curvature comes in only through the constitutive equation for the free energy and does not enter explicitly into the Euler-Lagrange equations. However, the Euler-Lagrange equations are influenced by surface geometry through the fact that the element of surface area in Eq. (46) is the volume form in a curved space. Consequently, the derivatives in the Euler-Lagrange equations are covariant derivatives.

The presuppositions necessary to derive the variational principle are summarized again.

(i) The specific external force is conservative: $\underline{f} = -\underline{\nabla} \gamma_s$.

(ii) The surrounding material has constant temperature $T^R$ and constant pressure $p^R$ in the bulk regions, and constant pressure $p_s^R$ along the curve $C$ which contacts the liquid crystal with the isotropic reservoir in the plane of the surface (see Fig. 3): $\underline{\underline{\Pi}} = 0$, $\underline{\underline{\Pi}}_s = 0$.

(iii) There are no couple stresses in the liquid crystal: $\underline{m}_s = 0$.

(iv) The film is at rest: $w^\perp = 0$.

(v) There is no material flux through the film: $(\underline{v} - \underline{w}) \cdot \underline{e} = 0$.

The evolution criterion has been derived for a two-dimensional system in contact with a reservoir. The temperature $T^R$ in the integrand of the global free energy $G$ is the constant temperature of the reservoir, and $p^R$ and $p_s^R$ are its constant pressures. The derivation of the evolution criterion shown here is possible, if only one reservoir is present. A system in contact with two reservoirs of different temperatures or even more complex situations with a temperature field on the contacting boundary are left to future investigations.

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