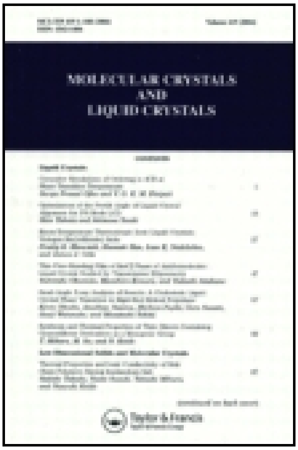

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Christina Papenfuss [a]

[a] Technische Universität Berlin, Institut für Mechanik, Straße des 17. Juni 135, 10623, Berlin, Germany

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Liquid Crystalline Surface Tension and Radius Dependence of the Internal Pressure in Liquid Crystalline Bubbles and Droplets

CHRISTINA PAPENFUSS

Technische Universität Berlin, Institut für Mechanik, Straße des 17. Juni 135, 10623 Berlin, Germany

The balance of surface momentum density is the equation relevant to describe capillary rise experiments as well as the radius-internal pressure relation in liquid crystalline bubbles and droplets. This equation involves the surface stress tensor. The surface stress tensor has been calculated from the Second Law of Thermodynamics. The normal stresses do not vanish. They have an influence in capillary rise experiments for measuring the surface tension: For simple liquids the easiest way to measure the surface tension is the determination of the hight of the liquid in a capillary and the contact angle of the liquid at the glass surface. In the case of simple liquids there is an algebraic relation between these quantities and surface tension. This is not the case for liquid crystals. There one has a differential equation relating surface tension to the measured quantities. This results in an influence of boundary conditions. Also the pressure-radius relation for smectic bubbles is predicted to be different from the relation for simple materials.

Keywords: surface tension; droplets; continuum theory

INTRODUCTION

Gibbs [1] introduced the notion of surface excess mass in order to take into account the mass density variation at a phase interface. This concept has been generalized and surface densities of other physical fields have been introduced [2]. For these surface densities balance equations have been derived [3]. This approach will be applied here to the interface liquid crystal - air. In case of liquid crystal surfaces two effects have to be taken into account: surface geometry and the liquid crystalline order. The geometry can be described by the curvature tensor or more easily by the mean and the Gaussian curvature, K_M and K_G. The variables for the liquid crystalline order are the alignment tensors a^k [4], in the simplest case only the second order alignment tensor $\underline{\underline{a}}$. The curvature and the alignment tensor are both relevant variables for all constitutive properties. So, for instance the free energy density depends on the alignment tensor and on the geometry. If the derivatives of the free energy with respect to the alignment tensor and to geometric variables do not vanish it can be shown, that the surface normal stress is not zero. This means that pulling the surface in the tangential direction there is a force not only tangential to the surface, but also a component normal to the surface. This is due to the coupling of orientational order and surface geometry. For the normal stresses an expression in terms of derivatives of the free energy density with respect to alignment tensor and geometrical variables can be derived , which is given in the appendix. The derivation of this expression uses the second law of thermodynamics.

CONSEQUENCES FOR THE MEASUREMENT OF SURFACE TENSION

The simplest way to measure the surface tension of a liquid is a capillary rise experiment. A capillary tube is dipped into a vessel with the liquid.

symbol	physical quantity
ρ_s	surface mass density
$\underline{v}$	material velocity in the bulk
$\underline{\underline{t}}_s$	surface stress tensor
$\underline{\underline{t}}$	stress tensor defined in the bulk
$\underline{f}$	acceleration due to external fields (gravitation)
f_s	surface specific internal energy
e	specific internal energy in the bulk
$\underline{\underline{g}}$	metric tensor (surface geometry)
$\underline{\tau}$	surface tangential vector
$\underline{e}$	surface normal vector

Depending on the surface tension of the liquid, the level of the liquid in the capillary is higher or lower than in the vessel and the liquid forms a convex or concave meniscus, respectively. The height h and the contact angle θ are measured. It is assumed that the meniscus has a spherical shape. Then

$$b^{\alpha}_{\alpha} = 2K_M = 2/R \quad , \tag{1}$$

where R is the radius of curvature of the meniscus. The equation relevant here is the balance of momentum. The balance of momentum can be split into equations for vector components tangential to the surface and normal to the surface. The differential equation for the normal component of momentum is:

$$\begin{aligned} \rho_s \frac{\partial w^{\perp}}{\partial t} &= -\rho_s w^{\gamma} w^{\perp}_{,\gamma} + \rho_s w^{\alpha}\left(w^{\perp}_{,\alpha} + w^{\gamma} b_{\gamma\alpha}\right) + \left(t^{\perp\alpha}_{s\ ,\alpha} + t^{\gamma\alpha}_{s} b_{\gamma\alpha}\right) - \\ &- \ [-t^{km} + \rho(v^k - w^k)(v^m - w^m)]e^m e^k - \rho_s f^k e^k = 0 \quad . \end{aligned} \tag{2}$$

In equilibrium we have $\underline{w} = 0$. In addition we define the position of the singular surface such that the surface excess mass vanishes. Equation (8) then reduces to

$$t^{\gamma\alpha}_{s} b_{\gamma\alpha} + [t^{km}]e^k e^m = 0 \quad . \tag{3}$$

For simple liquids the surface stress tensor is an isotropic surface tensor:

$$t^{\alpha\beta}_{s} = \frac{\gamma}{2} g^{\alpha\beta} \tag{4}$$

and the scalar coefficient γ is called surface tension. The bulk stress tensor is isotropic, i. e. $[t^{km}]e^k e^m = [p]$. The pressure difference is balanced by the gravitational force density on the liquid column. Therefore for simple liquids the surface tension is given by the expression

$$\gamma = \frac{1}{2} g h (\rho - \rho_0) \frac{R}{\cos\theta} \quad , \tag{5}$$

with ρ being the density of the liquid and ρ_0 the density of the air.

For the interface liquid crystal - air the situation is more difficult because of the nonvanishing normal stresses. The balance of normal component of momentum includes the normal stresses. If one defines the surface tension analogously to the case of simple liquids equation (5), these surface stresses include not only the scalar coefficient $\tilde{\gamma}$ with $t^{\alpha\beta}_{s} = (\tilde{\gamma}/2)g^{\alpha\beta}$ but also the normal stresses.

The tangential component of the balance of momentum in equilibrium is:

$$t_s^{\perp\alpha} b_\alpha^\beta - t_{s\ ,\alpha}^{\beta\alpha} - [t^{lm}] e^m \tau^{l\beta} - \tau^{l\beta} \rho_s f^l = 0 \quad . \tag{6}$$

Again we define the position of the surface such that surface excess mass vanishes ($\rho_s = 0$) and we assume that also in the presence of normal stresses the shape of the meniscus is spherical.

With the result on the tangential part of the stress tensor $t_s^{\alpha\beta} = \gamma g^{\alpha\beta}$ from the dissipation inequality and an isotropic bulk stress tensor $\underline{\underline{t}} = -p\underline{\underline{\delta}}$ we end up with the tangential component of the balance of momentum:

$$\frac{1}{R} t_s^{\perp\beta} - \left(\gamma g^{\alpha\beta}\right)_{,\alpha} = 0 \quad . \tag{7}$$

For the spherical geometry $g^{\alpha\beta}{}_{,\alpha} = 0$ and therefore

$$\frac{1}{R} t_s^{\perp\beta} - \gamma_,{}^{\beta} = 0 \quad . \tag{8}$$

The normal component of the balance of momentum yields

$$t_{s\ ,\alpha}^{\perp\alpha} + \frac{2\gamma}{R} + [p] = 0 \quad . \tag{9}$$

The first term in this equation is different from the case of simple liquids, where the normal stresses vanish.

The divergence of the normal stresses can be eliminated by means of equation (8):

$$t_{s\ ,\alpha}^{\perp\alpha} = \left(R\gamma^{,\alpha}\right)_{,\alpha} = R\left(\gamma\right)_{,\alpha}^{\ \alpha} \quad . \tag{10}$$

Finally we have a partial differential equation for the scalar coefficient γ (surface tension):

$$R\gamma_{,\alpha}^{\ \alpha} + \frac{2\gamma}{R} + [p] = 0 \quad , \tag{11}$$

where the second dervative of surface tension with respect to the surface coordinates appears. The pressure jump $[p]$ is measured by the hight of the liquid column and the Radius R of curvature of the meniscus is given experimentally in terms of the contact angle. To calculate the surface tension from these data, boundary conditions on the line C of contact with the glass capillary have to be given and the differential equation has to be solved.

Because of the rotation symmetry of the capillary it is a reasonable to assume that γ does not depend on the azimuthal angle ϕ. Then equation (11) simplifies to an ordinary differential equation:

$$\frac{\partial^2\gamma}{\partial\theta^2} + 2\gamma = -[p]R \quad . \tag{12}$$

Because of the rotation symmetry we must have $\gamma(\theta) = \gamma(-\theta)$. With boundary condition on the curve C

$$\gamma(\theta_0) = \gamma_0 \tag{13}$$

the solution is

$$\gamma(\theta) = C_1 \cos(\sqrt{2}\theta) - [p]R, \quad C_1 = \frac{\gamma(\theta_0) + [p]R}{\cos(\sqrt{2}\theta_0)} \quad . \tag{14}$$

Different boundary conditions γ_0 could be prepared experimentally by different surface treatment of the capillary. The different forms of surface alignment (planar or homeotropic) imposed this way should result in different values of surface tension on the curve C of contact of the meniscus with the glass capillary. As a consequence the surface tension calculated by (14) from the experimental data depends on the surface treatment of the capillary. This has been confirmed experimantally in [5].

There are other kinds of experiments, which can be performed in order to measure the surface tension: One can measure the force necessary to enlarge the In these experiments the liquid film is flat. Then the equations (3) and (6) for the normal- and the tangential component of the balance of momentum decouple. The normal stresses do not enter into equation (3), and we end up with the same algebraic equation for the surface tension as for simple fluids:

$$\gamma = -\frac{1}{2}[p]R \quad . \tag{15}$$

This way the coefficient γ can be measured easily. Knowing the coefficient γ, the coefficient C_1 in equation (14) can be determined from a capillary rise experiment: The hight h of the liquid column is measured in the middle of the meniscus ($\theta = 0$). Then C_1 is given by

$$C_1 = \gamma + [p]R \quad . \tag{16}$$

If the part of the solution (14) $C_1 \cos\sqrt{2}\theta$ is not taken into account in the interpretation of capillary rise experiments with liquid crystals, this leads to a wrong interpretation of the data.

THE PRESSURE RADIUS RELATION FOR LIQUID CRYSTALLINE BUBBLES

From the balance of momentum in equilibrium we find the following relation between the internal pressure within a liquid crystalline bubble and the radius of the bubble:

$$R\gamma_{,\alpha}^{\alpha} + \frac{2\gamma}{R} = -[p] \quad . \tag{17}$$

The term proportional to the radius does not appear for simple materials. The above relation results in an internal pressure decreasing more slowly with increasing radius than for simple materials.

CONCLUSIONS

In liquid crystals the normal stresses are nonzero. This leads to a differential equation relating the surface tension to the experimentally measurable quantities. The consequence is an influence of boundary conditions. This has been confirmed experimentally [5].

Another consequence of the nonvanishing normal stresses and the balance of momentum in equilibrium is a relation between radius and internal pressure in droplets and bubbles, which is modified compared to simple liquids.

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APPENDIX:

The stress tensor calculated from the free energy density f_s

From an exploitation of the second law of thermodynamics, taking into account all balance equations one can derive the following expressions for the tangential component of the stress tensor and the normal component [3] ($\underline{\tau}$ is a surface tangential vector, and $\underline{e}$ is the surface normal vector.)

$$t_s^{\alpha\beta} \;=\; g^{\alpha\beta}\rho_s^2\left[\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}\left(\frac{\partial f_s}{\partial T_s}-\eta_s\right)\frac{\partial\rho_s^{tot}}{\partial\rho_s}-\left(\frac{\partial f_s}{\partial\rho_s}\right)\right]$$

Here also an electric charge density ρ_s^{tot} has been taken into account.

Normal stresses are nonzero:

$$\begin{aligned}
& t_s^{\perp\beta} = -\rho_s\tau^{k\gamma}{}_{,\gamma}\tau^{k\beta}\left[\frac{\partial f_s}{\partial b_\alpha^\alpha}+(\eta_s-\frac{\partial f_s}{\partial T_s})\left(\frac{\partial\rho^{tot}}{\partial T_s}\right)^{-1}\frac{\partial\rho_s^{tot}}{\partial b_\alpha^\alpha}\right]+\\
+ \quad & 2\rho_s b_{\gamma\delta}\tau^{m\delta}\tau^{m\beta,\gamma}\left[\frac{\partial f_s}{\partial I_2}+\frac{\partial f_s}{\partial I_3}+\right.\\
+ \quad & \left.(\eta_s-\frac{\partial f_s}{\partial T_s})\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}\left(\frac{\partial\rho_s^{tot}}{\partial I^2}+\frac{\partial\rho_s^{tot}}{\partial I^3}\right)\right]+\\
+ \quad & \rho_s\left(e^{k,\beta}\tau^{k\,\gamma}_{\gamma,}+2b_\nu{}^\beta\tau^{l\nu}\tau^{l\gamma}{}_{,\gamma}-2b^\mu_\mu\tau^{l\beta}\tau^{l\gamma}{}_{,\gamma}+2b^\beta_\nu\tau^{l\nu}\tau^{l\gamma}{}_{,\gamma}\right)*\\
* \quad & \left(\frac{\partial f_s}{\partial I^1}+\left(\eta_s-\frac{\partial f_s}{\partial T_s}\right)\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}\frac{\partial\rho_s^{tot}}{\partial I^1}\right)\\
+ \quad & 2\rho_s\left(\tau^{k\beta,\mu}e_{k,\mu}+b^\mu_\gamma\tau^{l\beta}\tau^{l\gamma,\mu}\right)\left(\frac{\partial f_s}{\partial I^0}+\left(\eta_s-\frac{\partial f_s}{\partial T_s}\right)\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}\frac{\partial\rho_s^{tot}}{\partial I^0}\right)\\
+ \quad & 2\rho_s\left(b^{\beta\gamma}\tau^l_\gamma\tau^{l\delta}{}_{,\delta}+b^\gamma_\gamma\tau^{l\beta}\tau^{l\delta}{}_{,\delta}\right)\left(\frac{\partial f_s}{\partial I^1}+\left(\eta_s-\frac{\partial f_s}{\partial T_s}\right)\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}\frac{\partial\rho_s^{tot}}{\partial I^1}\right)\\
- \quad & 2\rho_s\left(-b^\gamma_\alpha\tau^k_\gamma\tau^{k\alpha,\beta}+b^\gamma_\alpha\tau^{l\alpha,\gamma}\tau^{l\beta}\right)\left(\frac{\partial f_s}{\partial I^0}+\left(\eta_s-\frac{\partial f_s}{\partial T_s}\right)\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}\frac{\partial\rho_s^{tot}}{\partial I^0}\right)\\
- \quad & 2a_s^{\perp\beta}\left(\rho_s\frac{\partial f_s}{\partial a_s^{\perp\perp}}+\frac{\partial\rho_s^{tot}}{\partial a_s^{\perp\perp}}\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}(\rho_s\eta_s-\rho_s\frac{\partial f_s}{\partial T_s})\right)+\\
+ \quad & a_s^{\perp\perp}\left(\rho_s\frac{\partial f_s}{\partial a_s^{\perp\beta}}+\frac{\partial\rho_s^{tot}}{\partial a_s^{\perp\beta}}\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}(\rho_s\eta_s-\rho_s\frac{\partial f_s}{\partial T_s})\right)-\\
- \quad & a_s^{\alpha\beta}\left(\rho_s\frac{\partial f_s}{\partial a_s^{\perp\alpha}}+\frac{\partial\rho_s^{tot}}{\partial a_s^{\perp\alpha}}\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}(\rho_s\eta_s-\rho_s\frac{\partial f_s}{\partial T_s})\right)+\\
+ \quad & 2a_s^{\perp\alpha}\left(\rho_s\frac{\partial f_s}{\partial a_s^{\alpha\beta}}+\frac{\partial\rho_s^{tot}}{\partial a_s^{\alpha\beta}}\left(\frac{\partial\rho_s^{tot}}{\partial T_s}\right)^{-1}(\rho_s\eta_s-\rho_s\frac{\partial f_s}{\partial T_s})\right)\quad .
\end{aligned}$$

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