Including boundary free energy

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1 Effect of surface free energy

Recently we have been observing that a low-twist-constant configuration in a cylindrical domain with strong homeotropic anchoring on the boundaries tends to exhibit a director structure which rotates out of the plane on the cylinder ends. This happens in an oscillatory fashion, and also increases the uniaxial scalar order parameter to be close to the physical limit of the Q-tensor. Hence, we are seeking to prevent this behavior in order to try to reproduce the chiral twist configuration. This is done by imposing a weak planar surface anchoring term on the cylinder ends.

In the paper by Fournier and Galatola they introduce two terms which they take to be minimal in imperically representing good planar anchoring behavior. The first term (weakly) imposes that Q must coincide with its projection on the substrate. The second term (wealy) imposes that the scalar order parameter on the surface is equal to some specified equilibrium value S_0. To this end, they define:

$$\tilde{Q} = Q - \frac{1}{3} S_0 I \tag{1}$$

The projection is given by:

$$\tilde{Q}^\perp = P \tilde{Q} P \tag{2}$$

with $P = I - \boldsymbol{\nu} \otimes \boldsymbol{\nu}$ and $\boldsymbol{\nu}$ a unit vector normal to the surface. The term that shows up in the surface free energy density is:

$$W_1 \left(\tilde{Q}_{ij} - \tilde{Q}_{ij}^\perp \right) \left(\tilde{Q}_{ij} - \tilde{Q}_{ij}^\perp \right) \tag{3}$$

To better understand this term, we expand eq. (2) in terms of Q:

$$\begin{aligned} P \left(Q - \frac{1}{3} S_0 I \right) P &= PQP - \frac{1}{3} S_0 P^2 \\ &= PQP - \frac{1}{3} S_0 P \end{aligned} \tag{4}$$

Then the difference with the projection onto the substrate:

$$\begin{aligned} \tilde{Q} - \tilde{Q}^\perp &= Q - \frac{1}{3} S_0 I - PQP + \frac{1}{3} S_0 P \\ &= Q - PQP - \frac{1}{3} S_0 \left(\boldsymbol{\nu} \otimes \boldsymbol{\nu} \right) \end{aligned} \tag{5}$$

Supposing $\boldsymbol{\nu}$ coincides with $\hat{\mathbf{z}}$ the effect of PQP is just to eliminate the third row and column of Q. This quantity (squared) is then minimized when the third row and column of Q are zero except for the $(3, 3)$ entry which contains $\frac{1}{3} S_0$. This is true for uniaxial nematics for which $\mathbf{n}$ is in the x-y plane and have scalar order parameter S_0.

The second term reads:

$$W_2 \left(\tilde{Q}_{ij} \tilde{Q}_{ij} - S_0^2 \right)^2 \tag{6}$$

In terms of Q one of the factors reads:

$$\begin{aligned}\left(Q_{ij}+\frac{1}{3}S_0\delta_{ij}\right)\left(Q_{ij}+\frac{1}{3}S_0\delta_{ij}\right)-S_0^2 &= Q_{ij}Q_{ij}+\frac{1}{3}S_0^2-S_0^2\\ &= Q_{ij}Q_{ij}-\tfrac{2}{3}S_0^2\end{aligned}\tag{7}$$

In general, in a bases in which Q is diagonalied, it reads:

$$Q=\begin{bmatrix}\frac{2}{3}S & 0 & 0\\ 0 & \left(P-\frac{1}{3}S\right) & 0\\ 0 & 0 & -\left(P+\frac{1}{3}S\right)\end{bmatrix}\tag{8}$$

With this general form we get:

$$Q_{ij}Q_{ij}=\frac{2}{3}S^2+2P^2\tag{9}$$

For a uniaxial system, the surface potential is minimized for $S=S_0$. It appears that these two conditions impose that $\hat{\mathbf{n}}$ lies in the plane orthogonal to $\hat{\boldsymbol{\nu}}$ and also that the scalar order parameter does not deviate too much from S_0.

2 Including surface free energy in equation of motion

The total free energy, including the surface term, reads:

$$F=\int_\Omega\left[f_{\text{bulk}}+f_{\text{elastic}}\right]dV+\int_{\partial\Omega}f_{\text{surf}}\,dS\tag{10}$$

By definition we have:

$$\begin{aligned}\delta F[Q,\delta Q]=&\left.\frac{d}{d\tau}F[Q+\tau\delta Q]\right|_{\tau=0}\\ =&\int_\Omega\left[\frac{\partial f_{\text{bulk}}}{\partial Q_{ij}}\delta Q_{ij}+\frac{\partial f_{\text{elastic}}}{\partial Q_{ij}}\delta Q_{ij}+\frac{\partial f_{\text{elastic}}}{\partial\left(\partial_k Q_{ij}\right)}\partial_k\delta Q_{ij}\right]dV+\int_{\partial\Omega}\frac{\partial f_{\text{surf}}}{\partial Q_{ij}}\delta Q_{ij}dS\\ =&\int_\Omega\left[\frac{\partial f_{\text{bulk}}}{\partial Q_{ij}}+\frac{\partial f_{\text{elastic}}}{\partial Q_{ij}}-\partial_k\frac{\partial f_{\text{elastic}}}{\partial\left(\partial_k Q_{ij}\right)}\right]\delta Q_{ij}\,dV+\int_{\partial\Omega}\left[\frac{\partial f_{\text{surf}}}{\partial Q_{ij}}+\frac{\partial f_{\text{elastic}}}{\partial\left(\partial_k Q_{ij}\right)}\nu_k\right]\delta Q_{ij}\,dS\end{aligned}\tag{11}$$

We have previously calculated each of these terms explicitly, save the derivative of the surface free energy. We do this now:

$$\begin{aligned}\frac{\partial f_{\text{surf}}}{\partial Q_{ij}}=&W_1\frac{\partial}{\partial Q_{ij}}\left[Q_{kl}-P_{km}Q_{mn}P_{nl}-\frac{1}{3}S_0\nu_k\nu_l\right]\left[Q_{kl}-P_{k\alpha}Q_{\alpha\beta}P_{\beta l}-\frac{1}{3}S_0\nu_k\nu_l\right]\\ &+W_2\frac{\partial}{\partial Q_{ij}}\left[Q_{kl}Q_{kl}-\frac{2}{3}S_0^2\right]^2\\ =&2W_1\left[\delta_{ik}\delta_{jl}-P_{km}\delta_{im}\delta_{jn}P_{nl}\right]\left[Q_{kl}-P_{k\alpha}Q_{\alpha\beta}P_{\beta l}-\frac{1}{3}S_0\nu_k\nu_l\right]\\ &+2W_2\left[Q_{kl}Q_{kl}-\frac{2}{3}S_0^2\right]2\delta_{ik}\delta_{jl}Q_{kl}\\ =&2W_1\left(\left[Q_{ij}-P_{i\alpha}Q_{\alpha\beta}P_{\beta j}-\frac{1}{3}S_0\nu_i\nu_j\right]-P_{ik}\left[Q_{kl}-P_{k\alpha}Q_{\alpha\beta}P_{\beta l}-\frac{1}{3}S_0\nu_k\nu_l\right]P_{lj}\right)\\ &+4W_2\left[Q_{kl}Q_{kl}-\frac{2}{3}S_0^2\right]Q_{ij}\\ =&2W_1\left[Q-PQP-\frac{1}{3}S_0\left(\boldsymbol{\nu}\otimes\boldsymbol{\nu}\right)\right]+4W_2\left[Q:Q-\frac{2}{3}S_0^2\right]Q\end{aligned}\tag{12}$$

where we have used the fact that $PP = P$ and that:

$$\begin{aligned} P\left(\boldsymbol{\nu}\otimes\boldsymbol{\nu}\right)P &= \left(I - \boldsymbol{\nu}\otimes\boldsymbol{\nu}\right)\left(\boldsymbol{\nu}\otimes\boldsymbol{\nu}\right)\left(I - \boldsymbol{\nu}\otimes\boldsymbol{\nu}\right) \\ &= \boldsymbol{\nu}\otimes\boldsymbol{\nu} - \boldsymbol{\nu}\otimes\boldsymbol{\nu} - \boldsymbol{\nu}\otimes\boldsymbol{\nu} + \boldsymbol{\nu}\otimes\boldsymbol{\nu} \\ &= 0 \end{aligned} \tag{13}$$

One problem remains, which is that the W_1 term is not necessarily traceless. To accommodate this formally, one introduces a Lagrange multiplier term of the form λQ_{ii} to the free energy. The result takes the form of just subtracting off I scaled by a third of the trace, which we calculate below:

$$\begin{aligned} \operatorname{tr}\left(Q - PQP - \frac{1}{3}S_0\left(\boldsymbol{\nu}\otimes\boldsymbol{\nu}\right)\right) &= \operatorname{tr}(Q) - \operatorname{tr}(PQ) - \frac{1}{3}S_0 \\ &= \operatorname{tr}(Q) - \operatorname{tr}(Q) + \operatorname{tr}\left(\left(\boldsymbol{\nu}\otimes\boldsymbol{\nu}\right)Q\right) - \frac{1}{3}S_0 \\ &= \delta_{ij}\nu_i\nu_k Q_{kj} - \frac{1}{3}S_0 \\ &= \boldsymbol{\nu}^T Q\boldsymbol{\nu} - \frac{1}{3}S_0 \end{aligned} \tag{14}$$

where we have used $PP = P$, and several properties of the trace. Plugging back in yields:

$$\frac{\partial f_{\text{surf}}}{\partial Q} = 2W_1\left[Q - PQP - \frac{1}{3}S_0\left(\boldsymbol{\nu}\otimes\boldsymbol{\nu}\right) - \frac{1}{3}\left(\boldsymbol{\nu}^T Q\boldsymbol{\nu} - \frac{1}{3}S_0\right)I\right] + 4W_2\left[Q : Q - \frac{2}{3}S_0^2\right]Q \tag{15}$$

for which the trace is zero.

Now, at each instant Q must be evolving in such a way that decreases F. If we take $-\partial Q/\partial t$ to be terms in brackets in eq. (11) in the bulk and on the surface respectively then $\delta F/\delta t \leq 0$ at all times. So then we end up with two coupled equations:

$$\frac{\partial Q}{\partial t} = -\frac{\partial f_{\text{bulk}}}{\partial Q} - \frac{\partial f_{\text{elastic}}}{\partial Q} + \nabla\cdot\frac{\partial f_{\text{elastic}}}{\partial\left(\nabla Q\right)} \qquad \text{(bulk)} \tag{16}$$

$$\frac{\partial Q}{\partial t} = -\frac{\partial f_{\text{surf}}}{\partial Q} - \boldsymbol{\nu}\cdot\frac{\partial f_{\text{elastic}}}{\partial\left(\nabla Q\right)} \qquad \text{(surface)} \tag{17}$$

$$\tag{18}$$

To simplify notation, take $T^Q = -\partial(f_{\text{bulk}} + f_{\text{elastic}})/\partial Q$ and $T^{\nabla Q} = \partial f_{\text{elastic}}/\partial(\nabla Q)$. Also take $T^s = -\partial f_{\text{surf}}/\partial Q$. Then these read:

$$\frac{\partial Q}{\partial t} = T^Q + \nabla\cdot T^{\nabla Q} \tag{19}$$

$$\frac{\partial Q}{\partial t} = T^s - \boldsymbol{\nu}\cdot T^{\nabla Q} \tag{20}$$

3 Discretizing in time

Define $T(Q, \nabla Q)$ to be the righthand side of eq. (19) or (20) depending on context. Then a semi-implicit time-discretization scheme looks like:

$$\frac{Q - Q_0}{\delta t} = \theta\, T(Q_0, \nabla Q_0) + (1-\theta)\, T(Q, \nabla Q) \tag{21}$$

where δt is the discrete time-step and θ is a parameter controlling how implicit vs. explicit the method is. For $\theta = 1$ it is explicit, $\theta = 0$ it is implicit, and $\theta = 1/2$ it is a Crank-Nicolson scheme. Since this is a nonlinear equation, we write a residual whose zeros we seek:

$$R(Q, \nabla Q) = Q - Q_0 - \delta t\left[\theta\, T(Q_0, \nabla Q_0) + (1-\theta)\, T(Q, \nabla Q)\right] \tag{22}$$

To use a Newton-Rhapson method, we must take the Gateaux derivative of R:

$$dR(Q, \nabla Q)\, \delta Q = \frac{d}{d\tau} \left[R(Q + \tau \delta Q, \nabla Q + \tau \nabla \delta Q) \right]_{\tau = 0} \tag{23}$$

Then, the Newton-Rhapson method reads:

$$dR\, \delta Q = -\alpha R \tag{24}$$

where $\alpha \leq 0$ is some stabilization constant, and this is a linear equation in δQ. Now, such an equation will apply separately to the surface and the bulk. To accommodate the surface terms with the finite element method, we write out eq. (24) explicitly for the surface terms:

$$\begin{aligned}
&\delta Q - \delta t\, (1 - \theta) \left[dT^s \delta Q - \boldsymbol{\nu} \cdot \left(dT^{\nabla Q} \delta Q \right) \right] = \\
&\quad - \alpha \left(Q - Q_0 - \delta t \left[\theta \left(T_0^s - \boldsymbol{\nu} \cdot T_0^{\nabla Q} \right) + (1 - \theta) \left(T^s - \boldsymbol{\nu} \cdot T^{\nabla Q} \right) \right] \right) \\
\implies &\delta t\, (1 - \theta)\, \boldsymbol{\nu} \cdot \left(dT^{\nabla Q} \delta Q \right) + \Big[\delta Q - \delta t\, (1 - \theta)\, dT^s \delta Q \Big] = \\
&\quad - \alpha\, \delta t\, \Big[\theta \boldsymbol{\nu} \cdot T_0^{\nabla Q} + (1 - \theta)\, \boldsymbol{\nu} \cdot T^{\nabla Q} \Big] - \alpha \left(Q - Q_0 - \delta t \left[\theta T_0^s + (1 - \theta)\, T^s \right] \right) \\
\implies &\delta t\, (1 - \theta) \left\langle \Phi, \boldsymbol{\nu} \cdot \left(dT^{\nabla Q} \delta Q \right) \right\rangle_{\partial\Omega} + \Big[\langle \Phi, \delta Q \rangle_{\partial\Omega} - \delta t\, (1 - \theta) \langle \Phi, dT^s \delta Q \rangle_{\partial\Omega} \Big] = \\
&\qquad - \alpha\, \delta t\, \left[\theta \left\langle \Phi, \boldsymbol{\nu} \cdot T_0^{\nabla Q} \right\rangle_{\partial\Omega} + (1 - \theta) \left\langle \Phi, \boldsymbol{\nu} \cdot T^{\nabla Q} \right\rangle_{\partial\Omega} \right] \\
&\qquad - \alpha \left(\langle \Phi, Q \rangle_{\partial\Omega} - \langle \Phi, Q_0 \rangle_{\partial\Omega} - \delta t \left[\theta \langle \Phi, T_0^s \rangle_{\partial\Omega} + (1 - \theta) \langle \Phi, T^s \rangle_{\partial\Omega} \right] \right)
\end{aligned} \tag{25}$$

where, in the last line, we have taken the inner product with an arbitrary test function Φ to get the weak form of the equation. We have also very deliberately separated out the terms corresponding to the elastic energy, as those will appear in the corresponding bulk equation as follows:

$$\begin{aligned}
&\delta Q - \delta t\, (1 - \theta) \left[dT^Q \delta Q + \nabla \cdot \left(dT^{\nabla Q} \delta Q \right) \right] = \\
&\quad - \alpha \left(Q - Q_0 - \delta t \left[\theta \left(T_0^Q + \nabla \cdot T_0^{\nabla Q} \right) + (1 - \theta) \left(T^Q + \nabla \cdot T^{\nabla Q} \right) \right] \right) \\
\implies &\langle \Phi, \delta Q \rangle - \delta t\, (1 - \theta) \left[\left\langle \Phi, dT^Q \delta Q \right\rangle - \left\langle \nabla \Phi, dT^{\nabla Q} \delta Q \right\rangle \right] - \delta t\, (1 - \theta) \left\langle \Phi, \boldsymbol{\nu} \cdot dT^{\nabla Q} \delta Q \right\rangle_{\partial\Omega} = \\
&- \alpha \left(\langle \Phi, Q \rangle - \langle \Phi, Q_0 \rangle - \delta t \left[\theta \left(\left\langle \Phi, T_0^Q \right\rangle - \left\langle \nabla \Phi, T_0^{\nabla Q} \right\rangle \right) + (1 - \theta) \left(\left\langle \Phi, T^Q \right\rangle - \left\langle \nabla, T^{\nabla Q} \right\rangle \right) \right] \right) \\
&\qquad\qquad + \alpha\, \delta t \left(\theta \left\langle \Phi, \boldsymbol{\nu} \cdot T_0^{\nabla Q} \right\rangle_{\partial\Omega} + (1 - \theta) \left\langle \Phi, \boldsymbol{\nu} \cdot T^{\nabla Q} \right\rangle_{\partial\Omega} \right)
\end{aligned} \tag{26}$$

Now, we may replace the surface integrals with other surface integrals by using eq. (25). Essentially we take eq. (25) to be a statement of Robin boundary conditions with the surface terms showing up in eq. (26) being the normal derivative terms. Making this substitution yields:

$$\begin{aligned}
&\langle \Phi, \delta Q \rangle - \delta t\, (1 - \theta) \left[\left\langle \Phi, dT^Q \delta Q \right\rangle - \left\langle \nabla \Phi, dT^{\nabla Q} \delta Q \right\rangle \right] + \langle \Phi, \delta Q \rangle_{\partial\Omega} - \delta t\, (1 - \theta) \langle \Phi, dT^s \delta Q \rangle_{\partial\Omega} = \\
&- \alpha \left(\langle \Phi, Q \rangle - \langle \Phi, Q_0 \rangle - \delta t \left[\theta \left(\left\langle \Phi, T_0^Q \right\rangle - \left\langle \nabla \Phi, T_0^{\nabla Q} \right\rangle \right) + (1 - \theta) \left(\left\langle \Phi, T^Q \right\rangle - \left\langle \nabla, T^{\nabla Q} \right\rangle \right) \right] \right) \\
&\qquad\qquad - \alpha \left(\langle \Phi, Q \rangle_{\partial\Omega} - \langle \Phi, Q_0 \rangle_{\partial\Omega} - \delta t \left[\theta \langle \Phi, T_0^s \rangle_{\partial\Omega} + (1 - \theta) \langle \Phi, T^s \rangle_{\partial\Omega} \right] \right)
\end{aligned} \tag{27}$$

We have already worked out the bulk terms of eq. (27) in detail, so now we focus on the surface terms:

$$T_{ij}^s(Q, \nabla Q) = -2W_1 \left[Q_{ij} - P_{ik} Q_{kl} P_{lj} - \frac{1}{3} S_0 \nu_i \nu_j - \frac{1}{3} \left(\nu_k \nu_l Q_{kl} - \frac{1}{3} S_0 \right) \delta_{ij} \right] - 4W_2 \left[Q_{kl} Q_{kl} - \frac{2}{3} S_0^2 \right] Q_{ij} \tag{28}$$

The derivative of this expression is:

$$dT^s(Q, \nabla Q)\, \delta Q_{ij} = -2W_1 \left[\delta Q_{ij} - P_{ik}\delta Q_{kl}P_{lj} - \frac{1}{3}\nu_k\nu_l\delta Q_{kl}\delta_{ij}\right] \\ - 4W_2 \left[2\delta Q_{kl}Q_{kl}Q_{ij} + Q_{kl}Q_{kl}\delta Q_{ij} - \frac{2}{3}S_0^2\delta Q_{ij}\right] \tag{29}$$

We must also look at the weak forms. The weak forms of Q, Q_0, and δQ are all obvious so we instead focus on the T^s boundary terms:

$$\langle \Phi, T^s\rangle_{\partial\Omega} = -2W_1 \left[\langle \Phi, Q\rangle_{\partial\Omega} - \langle \Phi, PQP\rangle_{\partial\Omega} - \tfrac{1}{3}S_0 \langle \Phi, \boldsymbol{\nu}\otimes\boldsymbol{\nu}\rangle_{\partial\Omega}\right] \\ - 4W_2 \left[\langle \Phi, (Q:Q)\, Q\rangle_{\partial\Omega} - \tfrac{2}{3}S_0^2 \langle \Phi, Q\rangle_{\partial\Omega}\right] \tag{30}$$

Here we have gotten rid of the term which is a multiple of δ_{ij} because Φ is traceless, and so the inner product is zero. Additionally:

$$\langle \Phi, dT^s\, \delta Q\rangle_{\partial\Omega} = -2W_1 \left[\langle \Phi, \delta Q\rangle_{\partial\Omega} - \langle \Phi, P\, \delta Q\, P\rangle_{\partial\Omega}\right] \\ - 4W_2 \left[2\langle \Phi, (\delta Q : Q)\, Q\rangle_{\partial\Omega} + \langle \Phi, (Q:Q)\, \delta Q\rangle_{\partial\Omega} - \frac{2}{3}S_0^2 \langle \Phi, \delta Q\rangle_{\partial\Omega}\right] \tag{31}$$

To finalize the weak form, we write:

$$\delta Q = \sum_\nu \delta Q_\nu \Phi_\nu \tag{32}$$

and stipulate that the above must be true for every test function Φ_μ. Then the weak form matrix equation reads:

$$\left\langle \Phi_\mu, dT^S \Phi_\nu\right\rangle_{\partial\Omega} = -2W_1 \left[\langle \Phi_\mu, \Phi_\nu\rangle_{\partial\Omega} - \langle \Phi_\mu, P\Phi_\nu P\rangle_{\partial\Omega}\right] \\ - 4W_2 \left[2\langle \Phi_\mu, (\Phi_\nu : Q)\, Q\rangle_{\partial\Omega} + \langle \Phi_\mu, (Q:Q)\, \Phi_\nu\rangle_{\partial\Omega} - \tfrac{2}{3}S_0^2 \langle \Phi_\mu, \Phi_\nu\rangle_{\partial\Omega}\right] \tag{33}$$

4 Writing out explicitly

The automatic code generation doesn't quite work, so we write out the bare minimum terms here as a check. Our basis is given explicitly by:

$$\Phi_1 = \begin{bmatrix} \phi & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\phi \end{bmatrix} \quad \Phi_2 = \begin{bmatrix} 0 & \phi & 0 \\ \phi & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \Phi_3 = \begin{bmatrix} 0 & 0 & \phi \\ 0 & 0 & 0 \\ \phi & 0 & 0 \end{bmatrix} \quad \Phi_4 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \phi & 0 \\ 0 & 0 & -\phi \end{bmatrix} \quad \Phi_5 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \phi \\ 0 & \phi & 0 \end{bmatrix} \tag{34}$$

So that Q is given by:

$$Q = \begin{bmatrix} Q_1 & Q_2 & Q_3 \\ Q_2 & Q_4 & Q_5 \\ Q_3 & Q_5 & -(Q_1 + Q_4) \end{bmatrix} \tag{35}$$

Then we calculate:

$$\begin{aligned} \langle \Phi_1, Q\rangle_{\partial\Omega} &= \int_{\partial\Omega} (2Q_1 + Q_4)\, \phi \\ \langle \Phi_2, Q\rangle_{\partial\Omega} &= \int_{\partial\Omega} 2Q_2\phi \\ \langle \Phi_3, Q\rangle_{\partial\Omega} &= \int_{\partial\Omega} 2Q_3\phi \\ \langle \Phi_4, Q\rangle_{\partial\Omega} &= \int_{\partial\Omega} (2Q_4 + Q_1)\, \phi \\ \langle \Phi_5, Q\rangle_{\partial\Omega} &= \int_{\partial\Omega} 2Q_5\phi \end{aligned} \tag{36}$$

And the inner product of the basis functions:

$$\begin{aligned}
\langle \Phi_i, \Phi_i \rangle_{\partial\Omega} &= \int_{\partial\Omega} 2\phi_i\phi_i \\
\langle \Phi_1, \Phi_4 \rangle_{\partial\Omega} &= \int_{\partial\Omega} \phi_1\phi_4 \\
\langle \Phi_4, \Phi_1 \rangle_{\partial\Omega} &= \int_{\partial\Omega} \phi_1\phi_4
\end{aligned} \tag{37}$$