Maier-Saupe free energy in weak form

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1 Introduction

Here we will find a PDE describing the time evolution equation of the Q-tensor from thermodynamic effects, according to the Maier-Saupe free energy. Then we will discretize time according to a general finite difference scheme. After this, we will put the resulting space-dependent equations into weak form. The result will be non-linear, so we will have to use Newton's method to compute the solution to the finite difference scheme.

2 Maier-Saupe free energy and equations of motion

2.1 Writing the free energy in terms of Q_{ij}

We begin by defining the tensor order parameter of the nematic system in terms of the probability distribution of the molecular orientation:

$$Q_{ij}(\mathbf{x}) = \int_{S^2} \left(\xi_i \xi_j - \tfrac{1}{3}\delta_{ij}\right) p(\xi; \mathbf{x}) d\xi \tag{1}$$

where $p(\xi; \mathbf{x})$ is the probability distribution of molecular orientation in local equilibrium at some temperature T and position $\mathbf{x}$. Note that this quantity is traceless and symmetric. Then the mean field free energy is given by:

$$F\left[Q_{ij}\right] = H\left[Q_{ij}\right] - T\Delta S \tag{2}$$

where H is the energy of the configuration, and ΔS is the entropy relative to the uniform distribution. We choose H to be:

$$H\left[Q_{ij}\right] = \int_\Omega \left\{-\alpha Q_{ij} Q_{ji} + f_e\left(Q_{ij}, \partial_k Q_{ij}\right)\right\} d\mathbf{x} \tag{3}$$

with α some interaction parameter and f_e the elastic free energy density. The entropy is given by:

$$\Delta S = -n k_B \int_\Omega \left(\int_{S^2} p(\xi; \mathbf{x}) \log\left[4\pi p(\xi; \mathbf{x})\right] d\xi \right) d\mathbf{x} \tag{4}$$

where n is the number density of molecules. Now, in general for a given Q_{ij} there is no unique $p(\xi; \mathbf{x})$ given by (1). Hence, there is no unique ΔS. To find the appropriate ΔS corresponding to some fixed Q_{ij}, we seek to maximize the entropy density for a fixed Q_{ij} via the method of Lagrange multipliers. This goes as follows:

$$\begin{aligned} \mathcal{L}[p] &= \Delta s[p] - \Lambda_{ij} Q_{ij}[p] \\ &= \int_{S^2} p(\xi) \left(\log\left[4\pi p(\xi)\right] - \Lambda_{ij}\left(\xi_i \xi_j - \tfrac{1}{3}\delta_{ij}\right) \right) d\xi \end{aligned} \tag{5}$$

Here we've taken the spatial dependence to be implicit, since each of these are local quantities, and we're minimizing them *locally*. So, define a variation in p given by:

$$p'(\xi) = p(\xi) + \varepsilon\eta(\xi) \tag{6}$$

Then we have that:

$$\begin{aligned}\frac{\delta\mathcal{L}}{\delta p} &= \left.\frac{d\mathcal{L}[p']}{d\varepsilon}\right|_{\varepsilon=0} \\ &= \left.\frac{d\mathcal{L}[p']}{dp'}\frac{dp'}{d\varepsilon}\right|_{\varepsilon=0} \\ &= \int_{S^2}\Big(\log\left[4\pi p(\xi)\right] - \Lambda_{ij}\left(\xi_i\xi_j - \tfrac{1}{3}\delta_{ij}\right) + 1\Big)\eta(\xi)d\xi\end{aligned} \tag{7}$$

Since this is for an arbitrary variation η, we must have that

$$\log\left[4\pi p(\xi)\right] - \Lambda_{ij}\left(\xi_i\xi_j - \tfrac{1}{3}\delta_{ij}\right) + 1 = 0 \tag{8}$$

Solving for $p(\xi)$ yields:

$$p(\xi) = \frac{1}{4\pi}\exp\left[-\left(\tfrac{1}{3}\Lambda_{ij}\delta_{ij} + 1\right)\right]\exp\left[\Lambda_{ij}\xi_i\xi_j\right] \tag{9}$$

However, $p(\xi)$ is a probability distribution, so we need to normalize it over the domain. When we do this, the constant factors out front cancel and we're just left with:

$$p(\xi) = \frac{\exp\left[\Lambda_{ij}\xi_i\xi_j\right]}{Z\left[\Lambda\right]} \tag{10}$$

$$Z\left[\Lambda\right] = \int_{S^2}\exp[\Lambda_{ij}\xi_i\xi_j]d\xi \tag{11}$$

Now p is uniquely defined in terms of the Lagrange multipliers Λ_{ij}. Plugging this back into the constraint equation (1) we get:

$$\begin{aligned}Q_{ij} &= \frac{1}{Z[\Lambda]}\left(\int_{S^2}\left(\xi_i\xi_j\exp[\Lambda_{kl}\xi_k\xi_l] - \tfrac{1}{3}\delta_{ij}\exp[\Lambda_{kl}\xi_k\xi_l]\right)d\xi\right) \\ &= \frac{1}{Z[\Lambda]}\left(\frac{\partial Z[\Lambda]}{\partial\Lambda_{ij}} - \tfrac{1}{3}\delta_{ij}Z[\Lambda]\right) \\ &= \frac{\partial\log Z}{\partial\Lambda_{ij}} - \tfrac{1}{3}\delta_{ij}\end{aligned} \tag{12}$$

This set of equations uniquely defines Λ_{ij} in terms of Q_{ij}, although the equation is not algebraically solvable. We may also plug (10) into (4) to get ΔS as a function of Λ_{ij} (and therefore implicitly of Q_{ij}):

$$\begin{aligned}\Delta S = -nk_B\int_\Omega\frac{1}{Z[\Lambda]}&\left(\int_{S^2}\exp[\Lambda_{ij}\xi_i\xi_j]\left(\log(4\pi) + \log(1/Z[\Lambda]) + \Lambda_{ij}\xi_i\xi_j\right)d\xi\right)d\mathbf{x} \\ = -nk_B\int_\Omega&\left(\log(4\pi) - \log(Z[\Lambda]) + \Lambda_{ij}\frac{\partial\log Z[\Lambda]}{\partial\lambda_{ij}}\right) \\ = -nk_B\int_\Omega&\left(\log(4\pi) - \log(Z[\Lambda]) + \Lambda_{ij}\left(Q_{ij} + \tfrac{1}{3}\delta_{ij}\right)\right)\end{aligned} \tag{13}$$

Further, we may explicitly write out the elastic free energy as:

$$f_e(Q_{ij}, \partial_k Q_{ij}) = L_1\left(\partial_k Q_{ij}\right)\left(\partial_k Q_{ij}\right) + L_2\left(\partial_j Q_{ij}\right)\left(\partial_k Q_{ik}\right) + L_3 Q_{kl}\left(\partial_k Q_{ij}\right)\left(\partial_l Q_{ij}\right) \tag{14}$$

2.2 Finding the equations of motion

Now, since Q_{ij} is traceless and symmetric, we need to use a Lagrange multiplier scheme so that there is an extra piece in our free energy:

$$f_l = -\lambda Q_{ii} - \lambda_i \epsilon_{ijk} Q_{jk} \tag{15}$$

To get a time evolution equation for Q, we just take the negative variation of the free energy density f with respect to each of them:

$$\partial_t Q_{ij} = -\frac{\partial f}{\partial Q_{ij}} + \partial_k \frac{\partial f}{\partial(\partial_k Q_{ij})} \tag{16}$$

Let's write out these terms explicitly. We start with the Maier-Saupe interaction term:

$$\begin{aligned} -\frac{\partial}{\partial Q_{ij}} \left(-\alpha Q_{kl} Q_{lk}\right) &= \alpha \delta_{ik} \delta_{jl} Q_{lk} + \alpha \delta_{il} \delta_{jk} Q_{kl} \\ &= 2\alpha Q_{ij} \end{aligned} \tag{17}$$

Now elastic energy:

$$\begin{aligned} -\frac{\partial}{\partial Q_{ij}} \left(L_3 Q_{kl} (\partial_k Q_{nm})(\partial_l Q_{nm})\right) &= -L_3 \delta_{ik} \delta_{jl} (\partial_k Q_{nm})(\partial_l Q_{nm}) \\ &= -L_3 (\partial_i Q_{nm})(\partial_j Q_{nm}) \end{aligned} \tag{18}$$

And the Lagrange multiplier terms:

$$\begin{aligned} -\frac{\partial}{\partial Q_{ij}} \left(-\lambda Q_{kk} - \lambda_k \epsilon_{klm} Q_{lm}\right) &= \lambda \delta_{ik} \delta_{jk} + \lambda_k \epsilon_{klm} \delta_{il} \delta_{jm} \\ &= \lambda \delta_{ij} + \lambda_k \epsilon_{kij} \end{aligned} \tag{19}$$

Now for the other elastic energy terms:

$$\begin{aligned} \partial_k \frac{\partial f}{\partial(\partial_k Q_{ij})} L_1 (\partial_l Q_{nm})(\partial_l Q_{nm}) &= L_1 \partial_k \left(\delta_{kl} \delta_{in} \delta_{jm} \partial_l Q_{nm} + \partial_l Q_{nm} \delta_{kl} \delta_{ik} \delta_{jm}\right) \\ &= 2 L_1 \partial_k \partial_k Q_{ij} \end{aligned} \tag{20}$$

And the L_2 term:

$$\begin{aligned} \partial_k \frac{\partial f}{\partial(\partial_k Q_{ij})} L_2 (\partial_m Q_{lm})(\partial_n Q_{ln}) &= L_2 \partial_k \left(\delta_{km} \delta_{il} \delta_{jm} (\partial_n Q_{ln}) + (\partial_m Q_{lm}) \delta_{kn} \delta_{il} \delta_{jn}\right) \\ &= L_2 \partial_k \left(\delta_{kj} (\partial_n Q_{in}) + \delta_{kj} (\partial_m Q_{im})\right) \\ &= 2 L_2 \partial_j (\partial_m Q_{im}) \end{aligned} \tag{21}$$

And finally the L_3 term:

$$\begin{aligned} \partial_k \frac{\partial f}{\partial(\partial_k Q_{ij})} L_3 Q_{np} (\partial_n Q_{lm})(\partial_p Q_{lm}) &= L_3 \partial_k Q_{np} \left(\delta_{kn} \delta_{il} \delta_{jm} (\partial_p Q_{lm}) + (\partial_n Q_{lm}) \delta_{kp} \delta_{il} \delta_{jm}\right) \\ &= L_3 \partial_k \left(Q_{kp} (\partial_p Q_{ij}) + Q_{nk} (\partial_n Q_{ij})\right) \\ &= 2 L_3 \partial_k \big(Q_{kn} (\partial_n Q_{ij})\big) \end{aligned} \tag{22}$$

Finally, we consider the entropy term:

$$\begin{aligned} -\frac{\partial}{\partial Q_{ij}} (-T \Delta s) &= -\frac{\partial}{\partial Q_{ij}} \left[-n k_B T \left(\log(4\pi) - \log(Z[\Lambda]) + \Lambda_{kl} (Q_{kl} + \tfrac{1}{3} \delta_{kl}\right)\right] \\ &= n k_B T \left(-\frac{\partial \log Z}{\partial \Lambda_{kl}} \frac{\partial \Lambda_{kl}}{\partial Q_{ij}} + \frac{\partial \Lambda_{kl}}{\partial Q_{ij}} \left(Q_{kl} + \tfrac{1}{3} \delta_{kl}\right) + \Lambda_{kl} \delta_{ik} \delta_{jl}\right) \\ &= n k_B T \left(-\left(Q_{kl} + \tfrac{1}{3} \delta_{kl}\right) \frac{\partial \Lambda_{kl}}{\partial Q_{ij}} + \frac{\partial \Lambda_{kl}}{\partial Q_{ij}} \left(Q_{kl} + \tfrac{1}{3} \delta_{kl}\right) + \Lambda_{ij}\right) \\ &= n k_B T \Lambda_{ij} \end{aligned} \tag{23}$$

Finally, we need to write down the Lagrange multipliers in terms of Q and its spatial derivatives. To do this, note that Q_{ij} is traceless and symmetric so that $\partial_t Q_{ij}$ is also traceless and symmetric. Hence, to find λ we just take negative $\frac{1}{3}$ the trace of the source term. This gives:

$$\begin{aligned}\lambda &= -\tfrac{1}{3}\left(-L_3(\partial_i Q_{nm})(\partial_i Q_{nm}) + 2L_2\partial_i(\partial_m Q_{im})\right) \\ &= \tfrac{1}{3}\left(L_3(\partial_i Q_{nm})(\partial_i Q_{nm}) - 2L_2\partial_i(\partial_m Q_{im})\right)\end{aligned} \tag{24}$$

where the rest of the terms are traceless. Now to find λ_k, we know that the anti-symmetric piece of any matrix can be given by:

$$\tfrac{1}{2}\left(A_{ij} - A_{ji}\right) \tag{25}$$

Further, the Lagrange multiplier term needs to cancel out the anti-symmetric piece:

$$\lambda_k \epsilon_{kij} = -\tfrac{1}{2}\left(A_{ij} - A_{ji}\right) \tag{26}$$

To solve for λ_k explicitly, we may calculate:

$$\begin{aligned}-\tfrac{1}{2}\epsilon_{lij}\left(A_{ij} - A_{ji}\right) &= \lambda_k \epsilon_{kij}\epsilon_{lij} \\ &= \lambda_k\left(\delta_{kl}\delta_{ii} - \delta_{ki}\delta_{il}\right) \\ &= 2\lambda_l\end{aligned} \tag{27}$$

Hence:

$$\begin{aligned}\lambda_l &= -\tfrac{1}{2}L_2\epsilon_{lij}\left(\partial_j(\partial_m Q_{im}) - \partial_i(\partial_m Q_{jm})\right) \\ &= \tfrac{1}{2}L_2\epsilon_{lij}\left(\partial_i(\partial_m Q_{jm}) - \partial_j(\partial_m Q_{im})\right)\end{aligned} \tag{28}$$

since the L_2 term is the only one that's anti-symmetric. The source term corresponding to this Lagrange multiplier piece is then given by:

$$\begin{aligned}\tfrac{1}{2}L_2\big((\partial_k\partial_n Q_{mn}) - (\partial_m\partial_n Q_{kn})\big)\epsilon_{lkm}\epsilon_{lij} &= \tfrac{1}{2}L_2\big((\partial_k\partial_n Q_{mn}) - (\partial_m\partial_n Q_{kn})\big)\left(\delta_{ki}\delta_{mj} - \delta_{kj}\delta_{mi}\right) \\ &= \tfrac{1}{2}L_2\big((\partial_i\partial_n Q_{jn}) - (\partial_j\partial_n Q_{in})\big) - \tfrac{1}{2}L_2\big((\partial_j\partial_n Q_{in}) - (\partial_i\partial_n Q_{jn})\big) \\ &= L_2\big((\partial_i\partial_n Q_{jn}) - (\partial_j\partial_n Q_{in})\big)\end{aligned} \tag{29}$$

Hence, the total equation of motion is:

$$\begin{aligned}\partial_t Q_{ij} &= 2\alpha Q_{ij} - L_3(\partial_i Q_{nm})(\partial_j Q_{nm}) + \tfrac{1}{3}\left(L_3(\partial_k Q_{nm})(\partial_k Q_{nm}) - 2L_2(\partial_k\partial_m Q_{km})\right)\delta_{ij} \\ &\qquad + L_2\big((\partial_i\partial_n Q_{jn}) - (\partial_j\partial_n Q_{in})\big) + nk_BT\Lambda_{ij} \\ &\qquad\qquad + 2L_1\partial_k\partial_k Q_{ij} + 2L_2(\partial_j\partial_m Q_{im}) + 2L_3\partial_k\big(Q_{kn}(\partial_n Q_{ij})\big) \\ &= 2\alpha Q_{ij} - L_3(\partial_i Q_{nm})(\partial_j Q_{nm}) + nk_BT\Lambda_{ij} \\ &\quad + 2L_1\partial_k\partial_k Q_{ij} + L_2\left((\partial_j\partial_m Q_{im}) + (\partial_i\partial_m Q_{jm})\right) + 2L_3\partial_k\big(Q_{kn}(\partial_n Q_{ij})\big) \\ &\qquad + \tfrac{1}{3}\left(L_3(\partial_k Q_{nm})(\partial_k Q_{nm}) - 2L_2(\partial_k\partial_m Q_{km})\right)\delta_{ij} \\ &= F_{ij}\left(Q_{ij}; \partial_k Q_{ij}; \partial_l\partial_k Q_{ij}\right)\end{aligned} \tag{30}$$

One can see that F_{ij} is both symmetric and traceless by virtue of Q_{ij} being traceless and symmetric.

3 Numerical scheme

3.1 Time discretization

To numerically solve this equation, we use Rothe's method to discretize the time dependence before the spatial dependence. To this end, we introduce the following finite difference scheme. For n the number of the current time step, call:

$$k = t_n - t_{n-1} \tag{31}$$

$$\partial_t Q_{ij} \to \frac{Q_{ij}^n - Q_{ij}^{n-1}}{k} \tag{32}$$

$$F_{ij} \to \left[\theta F_{ij}^n + (1-\theta) F_{ij}^{n-1}\right] \tag{33}$$

where F_{ij}^n is just F_{ij} with Q_{ij} evaluated at timestep n. Here $\theta = 0$ corresponds to an explicit Euler method, while $\theta = 1$ corresponds to an implicit Euler method. Also, $\theta = 1/2$ corresponds to a Crank-Nicolson method – we leave it undefined so that we may play with it later. The time-discretized equation is thus:

$$\begin{aligned} G_{ij}\left(Q_{ij}^n; \partial_k Q_{ij}^n; \partial_l \partial_k Q_{ij}^n\right) &= k\left[\theta F_{ij}^n + (1-\theta) F_{ij}^{n-1}\right] - Q_{ij}^n + Q_{ij}^{n-1} \\ &= 0 \end{aligned} \tag{34}$$

3.2 Space discretization

To turn this into a finite element problem, we introduce a scalar residual function:

$$R\left(Q_{ij}^n; \partial_k Q_{ij}^n; \partial_l \partial_k Q_{ij}^n\right) = \int_\Omega G_{ij} \phi_{ij} = 0 \tag{35}$$

where ϕ_{ij} is any test function. We can write the expression for F_{ij}^n out explicitly as follows:

$$\begin{aligned} \int_\Omega F_{ij}^n \phi_{ij} = 2\alpha \int_\Omega Q_{ij}\phi_{ij} - L_3 \int_\Omega (\partial_i Q_{nm})(\partial_j Q_{nm})\phi_{ij} + n k_B T \int_\Omega \Lambda_{ij}\phi_{ij} \\ + 2L_1 \int_{\partial\Omega} n_k \partial_k Q_{ij} \phi_{ij} - 2L_1 \int_\Omega (\partial_k Q_{ij})(\partial_k \phi_{ij}) + L_2 \int_{\partial\Omega} n_m \partial_j Q_{im} \phi_{ij} \\ - L_2 \int_\Omega (\partial_j Q_{im})(\partial_m \phi_{ij}) + L_2 \int_{\partial\Omega} n_m (\partial_i Q_{jm})\phi_{ij} - L_2 \int_\Omega (\partial_i Q_{jm})(\partial_m \phi_{ij}) \\ + 2L_3 \int_{\partial\Omega} n_k Q_{kn}(\partial_n Q_{ij})\phi_{ij} - 2L_3 \int_\Omega Q_{kn}(\partial_n Q_{ij})(\partial_k \phi_{ij}) + \tfrac{1}{3} L_3 \int_\Omega (\partial_k Q_{nm})(\partial_k Q_{nm})\phi_{ii} \\ - \tfrac{2}{3} L_2 \int_{\partial\Omega} n_k (\partial_m Q_{km})\phi_{ii} + \tfrac{2}{3} L_2 \int_\Omega (\partial_m Q_{km})(\partial_k \phi_{ii}) \end{aligned} \tag{36}$$

Now, since Q_{ij} is traceless and symmetric, we only have five independent degrees of freedom. We label as follows:

$$Q_{ij} = \begin{bmatrix} Q_1 & Q_2 & Q_3 \\ Q_2 & Q_4 & Q_5 \\ Q_3 & Q_5 & -(Q_1 + Q_4) \end{bmatrix} \tag{37}$$