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:

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

And the L_2 term:

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

And finally the L_3 term:

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

Finally, we consider the entropy term:

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

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:

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

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:

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

This anti-symmetric part will be exactly the Lagrange multiplier term:

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

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:

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

since the L_2 term is the only one that's anti-symmetric. Hence, the total equation of motion is:

$$\begin{aligned} \partial_t Q_{ij} = 2\alpha Q_{ij} - L_3(\partial_i Q_{nm})(\partial_j Q_{nm}) + \tfrac{1}{3}\left(L_3(\partial_k Q_{nm})(\partial_k Q_{nm}) - 2L_2(\partial_k\partial_m Q_{km})\right)\delta_{ij} \\ + \tfrac{1}{2}L_2\big((\partial_m\partial_n Q_{kn}) - (\partial_k\partial_n Q_{kn})\big)\epsilon_{lkm}\epsilon_{lij} + nk_BT\Lambda_{ij} \\ + 2L_1\partial_k\partial_k Q_{ij} + 2L_2(\partial_j\partial_m Q_{im}) + 2L_3\partial_k\big(Q_{kn}(\partial_n Q_{ij})\big) \end{aligned} \tag{29}$$

3 Numerical scheme

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

$$Q_{ij} = \begin{bmatrix} Q_1 & Q_2 & Q_3 \\ Q_2 & Q_4 & Q_5 \\ Q_3 & Q_5 & -(Q_1 + Q_4) \end{bmatrix} \tag{30}$$