

Maier-Saupe free energy in weak form

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1 Introduction

Here we will find the time evolution equation according to the Maier-Saupe free energy, and then put it into weak form so that it can be solved by a finite element method.

2 Maier-Saupe free energy and equations of motion

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

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

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:

$$F[Q_{ij}] = H[Q_{ij}] - T\Delta S \quad (2)$$

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

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

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

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

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:

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

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:

$$p'(\xi) = p(\xi) + \varepsilon \eta(\xi) \quad (6)$$

Then we have that:

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

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

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

Solving for $p(\xi)$ yields:

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

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:

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

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

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

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

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}):

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

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

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

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:

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

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

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

Now elastic energy:

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

And the Lagrange multiplier terms:

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

Now for the other elastic energy terms:

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

And the L_2 term:

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

And finally the L_3 term:

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

Finally, we consider the entropy term:

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

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:

$$\lambda = -\frac{1}{3} (-L_3 (\partial_i Q_{nm}) (\partial_i Q_{nm}) + 2L_2 \partial_i (\partial_m Q_{im})) \quad (24)$$

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:

$$\frac{1}{2} (A_{ij} - A_{ji}) \quad (25)$$

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

$$\lambda_k \epsilon_{kij} = -\frac{1}{2} (A_{ij} - A_{ji}) \quad (26)$$

To solve for λ_k explicitly, we may calculate:

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

Hence:

$$\lambda_l = -\frac{1}{2} L_2 \epsilon_{lij} (\partial_j (\partial_m Q_{im}) - \partial_i (\partial_m Q_{jm})) \quad (28)$$

since the L_2 term is the only one that's anti-symmetric.

Hence, the total equation of motion is:

$$\begin{aligned} \partial_t Q_{ij} &= 2\alpha Q_{ij} - L_3 (\partial_i Q_{nm}) (\partial_j Q_{nm}) + \frac{1}{3} (L_3 (\partial_k Q_{nm}) (\partial_k Q_{nm}) - 2L_2 (\partial_k \partial_m Q_{km})) \delta_{ij} \\ &\quad + \frac{1}{2} L_2 ((\partial_m \partial_n Q_{kn}) - (\partial_k \partial_n Q_{kn})) \epsilon_{lkm} \epsilon_{lij} + nk_B T \Lambda_{ij} \\ &\quad + 2L_1 \partial_k \partial_k Q_{ij} + 2L_2 (\partial_j \partial_m Q_{im}) + 2L_3 \partial_k (Q_{kn} (\partial_n Q_{ij})) \end{aligned} \quad (29)$$

To put this into weak form, we just integrate against

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

We label as follows:

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