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:

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

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:

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

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:

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

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:

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

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

$$Q_{ij} = \begin{bmatrix} Q_1 & Q_2 & Q_3 \\ Q_2 & Q_4 & Q_5 \\ Q_3 & Q_5 & -(Q_1+Q_2)\end{bmatrix} \tag{15}$$

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

$$\partial_t Q_i = -\frac{\delta f}{\delta Q_i} \tag{16}$$

where here we are thinking of Q as a vector of each of the independent parameters.