Diblock copolymer melt on a general curved surface: finite element computation

Kai Jiang

November 6, 2016

1 Self-consistent field theory (SCFT) on a general curved surface

Consider n AB diblock copolymers with the polymerization of N confined on a curved surface with a total surface area S. The volume fraction of A block is f and the two blocks disfavor with each other characterized by the Flory-Huggins parameter χ. Within mean-field approximation, the free energy density of this system in the unit of k_BT can be written as

$$\frac{F}{nk_BT} = \frac{1}{S}\int d\mathbf{s}\left\{-w_+(\mathbf{s}) + \frac{w_-^2(\mathbf{s})}{\chi N}\right\} - \log Q[w_+(\mathbf{s}), w_-(\mathbf{s})]$$

In the above equation, χ is the Flory-Huggins parameter to describe the interaction between segments A and B. $w_-(\mathbf{s})$ and $w_+(\mathbf{s})$ are the fluctuating pressure and exchange chemical potential fields, respectively. The pressure field enforces the local incompressibility, while the exchange chemical potential is conjugate to the density operators. Q is the single chain partition functional subjected to the fields w_+ and w_-. $d\mathbf{s}$ is the element of the surface. First-order variations of the free energy functional with respect to the fields will lead to the following self-consistent field (SCF) equations,

$$\phi_A(\mathbf{s}) + \phi_B(\mathbf{s}) - 1 = 0, \tag{1}$$

$$\frac{2w_-(\mathbf{s})}{\chi N} - [\phi_A(\mathbf{s}) - \phi_B(\mathbf{s})] = 0, \tag{2}$$

$$Q = \frac{1}{S}\int d\mathbf{s}\, q(\mathbf{s}, 1), \tag{3}$$

$$\phi_A(\mathbf{s}) = \frac{1}{Q}\int_0^f dt\, q(\mathbf{s}, t) q^\dagger(\mathbf{s}, 1-t), \tag{4}$$

$$\phi_B(\mathbf{s}) = \frac{1}{Q}\int_f^1 dt\, q(\mathbf{s}, t) q^\dagger(\mathbf{s}, 1-t). \tag{5}$$

$\phi_A(\mathbf{s})$ and $\phi_B(\mathbf{s})$ are A and B monomer densities. The forward propagator $q(\mathbf{s}, t)$ represents the probability weight that the chain of contour length t has its end at surface position $\mathbf{s}$, where the variable t is used to parameterize each copolymer chain. $t = 0$ represents the tail of the A block and $t = f$ is the junction between the A and B blocks. From the flexible Gaussian chain model, the forward propagator $q(\mathbf{s},t)$ satisfies the modified diffusion equation

$$
\begin{aligned}
&\frac{\partial}{\partial s}q(\mathbf{s},t) = [\nabla^2_{LB} - w(\mathbf{s})]q(\mathbf{s},t),\\
&q(\mathbf{s},0) = 1,\\
&w(\mathbf{s}) = \begin{cases} w_A(\mathbf{s}) = w_+(\mathbf{s}) - w_-(\mathbf{s}), & 0 \le t \le f,\\ w_B(\mathbf{s}) = w_+(\mathbf{s}) + w_-(\mathbf{s}), & f \le t \le 1,\end{cases}
\end{aligned}
\tag{6}
$$

where ∇^2_{LB} is the Laplace-Beltrami operator which is actually the divergence operator for the curved surface. The backward propagator $q^\dagger(\mathbf{u},t)$, which represents the probability weight from $t=1$ to $t=0$, satisfies

$$
\begin{aligned}
&\frac{\partial}{\partial s}q^\dagger(\mathbf{s},t) = [\nabla^2_{LB} - w^\dagger(\mathbf{s})]q(\mathbf{s},t),\\
&q^\dagger(\mathbf{s},0) = 1,\\
&w^\dagger(\mathbf{s}) = \begin{cases} w_B(\mathbf{s}) = w_+(\mathbf{s}) + w_-(\mathbf{s}), & 0 \le t \le 1-f,\\ w_A(\mathbf{s}) = w_+(\mathbf{s}) - w_-(\mathbf{s}), & 1-f \le t \le 1,\end{cases}
\end{aligned}
\tag{7}
$$

2 Numerical methods

Self-consistent iterative procedure

Step 1 Given initial estimations of fields $w_\pm(\mathbf{s})$;

Step 2 Compute forward (backward) propagator operators $q(\mathbf{s},t)$ and $q^\dagger(\mathbf{s},t)$ on a general curved surface (see Sec.);

Step 3 Obtain Q, $\phi_A(\mathbf{s})$ and $\phi_B(\mathbf{s})$ by integral equations (see Sec.), and calculate the free energy density F/nk_BT;

Step 4 Update fields $w_+(\mathbf{s})$ and $w_-(\mathbf{s})$ using some iterative methods (see Sec.);

Step 5 Goto **Step 2** until the free energy density does not change or SCF equations are satisfied.

2.1 PDE: full discretization

$$
\frac{\partial}{\partial t}q(\mathbf{s},t) = [\nabla^2_{LB} - w(\mathbf{s})]q(\mathbf{s},t) \tag{8}
$$

2.1.1 Finite element discretization with explicit Euler method

$$\frac{q^{n+1}(\mathbf{s}) - q^n(\mathbf{s})}{\tau} = [\nabla^2 - w(\mathbf{s})]q^n(\mathbf{s}) \tag{9}$$

i.e.,

$$q^{n+1}(\mathbf{s}) = [\tau\nabla^2 - \tau w(\mathbf{s}) + 1]q^n(\mathbf{s}) \tag{10}$$

Given a test function $v \in V$, we can consider the weak form

$$(q^{n+1}, v) = -\tau(\nabla q^n, \nabla v) - \tau(wq^n, v) + (q^n, v) \tag{11}$$

Using the finite dimensionally $P1$ space V_N, $v(\mathbf{s}) = \sum_{i=1}^N v_i\psi_i(\mathbf{s})$, $q^n(\mathbf{s}) = \sum_{j=1}^N q_j^n\psi_j(\mathbf{s})$, and $w(\mathbf{s}) = \sum_{l=1}^N w_l\psi_l(\mathbf{s})$.

The weak form becomes

$$\left(\sum_{j=1}^N q_j^{n+1}\psi_j, \psi_i\right) = -\tau\left(\sum_{j=1}^N q_j^n\nabla\psi_j, \nabla\psi_i\right) - \tau\left([\sum_{l=1}^N w_l\psi_l][\sum_{j=1}^N q_j^n\psi_j], \psi_i\right) + \left(\sum_{j=1}^N q_j^n\psi_j, \psi_i\right) \tag{12}$$

$i = 1, 2, \ldots, N$.

$$M\mathbf{q}^{n+1} = -\tau A\mathbf{q}^n - \tau K\mathbf{q}^n + M\mathbf{q}^n \tag{13}$$

where

$$M_{ij} = (\psi_i, \psi_j) \tag{14}$$

$$A_{ij} = (\nabla\psi_i, \nabla\psi_j) \tag{15}$$

$$K_{ij} = \sum_{l=1}^N w_l\Gamma_{ijl}, \qquad \Gamma_{ijk} = \int_\Omega d\mathbf{s}\,\psi_l\psi_j\psi_i \tag{16}$$

In practice implementation,

$$\mathbf{q}^{n+1} = [-\tau(\tilde{M})^{-1}(A + K) + I\,]\mathbf{q}^n \tag{17}$$

xxxx (TBA)

2.2 Integral formula

2.2.1 Integral formula along t-direction

A fourth-order integral formula can be used to approximate t-direction integral equations

$$\int_0^{n_t} dt\, f(t) = \Delta t\left\{-\frac{5}{8}(f_0 + f_{n_t}) + \frac{1}{6}(f_1 + f_{n_t-1}) - \frac{1}{24}(f_2 + f_{n_t-2}) + \sum_{j=0}^{n_t} f_j\right\}. \tag{18}$$

2.2.2 Surface integral $\int d\mathrm{s}$ (TBA)

2.3 Iterative method

$$
\begin{aligned}
w_+^{k+1}(\mathbf{s}) &= w_+^k(\mathbf{s}) + \lambda_+[\phi_A^k(\mathbf{s}) + \phi_B^k(\mathbf{s}) - 1] \\
w_-^{k+1}(\mathbf{s}) &= w_-^k(\mathbf{s}) - \lambda_- \left[\frac{2w_-(\mathbf{s})}{\chi N} - [\phi_A(\mathbf{s}) - \phi_B(\mathbf{s})]\right]
\end{aligned} \tag{19}
$$