

Supporting Information

Cylindrical inclusions in a copolymer membrane

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Self-consistent field theory for polymer systems

The present system consists of AB diblock copolymers and A homopolymers. In the SCFT,¹⁻³ the problem of many interacting chains is reduced to one of a single noninteracting polymer in external (mean) fields, created by the other chains. The fundamental quantity to be calculated in mean field studies is the polymer segment probability distribution function, $q(\mathbf{r}, s)$, representing the probability of finding segment s at position \mathbf{r} . The probability, $q(\mathbf{r}, s)$, satisfies the usual modified diffusion equation for the flexible polymer chains with the Gaussian statistics. For the copolymer amphiphile, it is

$$\frac{\partial q_a(\mathbf{r}, s)}{\partial s} = \begin{cases} R_g^2 \nabla^2 q_a(\mathbf{r}, s) - w_H(\mathbf{r}) q_a(\mathbf{r}, s), & \text{if } s < f \\ R_g^2 \nabla^2 q_a(\mathbf{r}, s) - w_T(\mathbf{r}) q_a(\mathbf{r}, s), & \text{if } s > f \end{cases} \quad (1)$$

with the initial condition $q_a(\mathbf{r}, 0) = 1$. Because the two ends of the copolymer are distinct, a second distribution function $q_a^+(\mathbf{r}, s)$ is defined. It satisfies the same diffusion equation (1) with the right-hand side multiplied by -1 , and the initial condition, $q_a^+(\mathbf{r}, N) = 1$.

The homopolymer only requires one end-segment distribution function, $q_S(\mathbf{r}, s)$, with the initial condition, $q_S(\mathbf{r}, 0) = 1$. It satisfies

$$\frac{\partial q_S(\mathbf{r}, s)}{\partial s} = R_g^2 \nabla^2 q_S(\mathbf{r}, s) - w_S(\mathbf{r}) q_S(\mathbf{r}, s) \quad (2)$$

The full partition function for a copolymer molecule acted upon by the mean field is

$$Q_a = \int d\mathbf{r} q_a(\mathbf{r}, s) q_a^+(\mathbf{r}, s) \quad (3)$$

and that for a homopolymer is

$$Q_S = \int d\mathbf{r} q_S(\mathbf{r}, s)q_S(\mathbf{r}, N - s) \quad (4)$$

In the grand-canonical ensemble, the segment concentrations are given by

$$\phi_H(\mathbf{r}) = \exp\left(\frac{\mu}{k_B T}\right) \int_0^f ds q_a(\mathbf{r}, s)q_a^+(\mathbf{r}, s) \quad (5)$$

$$\phi_T(\mathbf{r}) = \exp\left(\frac{\mu}{k_B T}\right) \int_f^1 ds q_a(\mathbf{r}, s)q_a^+(\mathbf{r}, s) \quad (6)$$

$$\phi_S(\mathbf{r}) = \int_0^1 ds q_S(\mathbf{r}, s)q_S(\mathbf{r}, 1 - s) \quad (7)$$

Within the SCFT approximation, the free energy of the system is given by eq (3) in the paper. The field configurations corresponding to stationary points of \mathcal{F} , satisfy the following set of coupled equations:

$$w_H(\mathbf{r}) = \chi N \phi_T(\mathbf{r}) + \xi(\mathbf{r}) \quad (8)$$

$$w_T(\mathbf{r}) = \chi N [\phi_H(\mathbf{r}) + \phi_S(\mathbf{r})] + \xi(\mathbf{r}) \quad (9)$$

$$w_S(\mathbf{r}) = \chi N \phi_T(\mathbf{r}) + \xi(\mathbf{r}) \quad (10)$$

$$\phi_0(\mathbf{r}) = \phi_H(\mathbf{r}) + \phi_T(\mathbf{r}) + \phi_S(\mathbf{r}) \quad (11)$$

The above non-linear equations can be solved numerically by a real space combinatorial screening algorithm.^{4, 5} The algorithm consists of defining a uniform grid with resolution $\Delta x = \Delta z = 0.1R_g$ within the simulation cell, generating the initial values of the potential fields randomly. Using a Crank-Nicholson scheme and an alternating-direction implicit (ADI) method,⁶ the diffusion equations are then integrated on the two-dimensional lattice with appropriate boundary conditions. Next, the eqs (5)-(7) are evaluated to obtain new expressions for the species volume fractions. The final step is to update the potential fields using eqs (8)-(10) by means of a linear mix of new and old solutions. These iterations are continued until incompressibility eq (11) is satisfied within acceptable tolerance of 10^{-4} .

Various contributions to free energy

The various contributions to F are given by⁷⁻⁹

$$\frac{NU}{\rho_0 k_B TV} = \frac{1}{V} \int d\mathbf{r} \{ \chi N \phi_T(\mathbf{r}) [\phi_H(\mathbf{r}) + \phi_S(\mathbf{r})] + H(\mathbf{r}) [\phi_H(\mathbf{r}) + \phi_S(\mathbf{r}) - \phi_T(\mathbf{r})] \} \quad (12)$$

$$\frac{NS_s}{\rho_0 k_B V} = \frac{1}{V} \int d\mathbf{r} [w_S(\mathbf{r}) \phi_S(\mathbf{r})] - \overline{\phi_S} \ln \left[\frac{V \overline{\phi_S}}{Q_S} - 1 \right] \quad (13)$$

$$\frac{NS_a}{\rho_0 k_B V} = \frac{1}{V} \int d\mathbf{r} [w_H(\mathbf{r}) \phi_H(\mathbf{r}) + w_T(\mathbf{r}) \phi_T(\mathbf{r})] - \overline{\phi_a} \ln \left[\frac{V \overline{\phi_a}}{Q_a} - 1 \right] \quad (14)$$

$$\frac{N \mu n_a}{\rho_0 k_B TV} = \frac{N \mu \overline{\phi_a}}{\rho_0 k_B TV} \quad (15)$$

where the quantities denoted by an over-bar are the volume-averaged copolymer (amphiphile) and homopolymer (solvent) concentrations.

References

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