Supporting Information: Entropic effects in solvent-free bidisperse polymer brushes investigated using density-functional theories

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The Self-Consistent Field Formalism for Homopolymer Brushes

The polymer SCFT formalism of ref 1 is reviewed for homopolymer brushes in the absence of other polymer matrices. The system schematic is shown in the lower panel of Figure 1(a), where the two parallel walls are separated by H. In the absence of solvent, the intervening polymers would uniformly fill the inter-wall space. Therefore, the total volume fraction of the polymers should satisfy the incompressibility condition,

$$\phi(z) + \phi(-z) = 1. \tag{S1}$$

The SCFT elastic free energy functional per chain in the system has the following form:

$$\frac{\mathcal{F}}{k_B T} = \bar{\phi}\left(\ln\frac{\bar{\phi}\mathcal{V}}{Q} - 1\right) - \frac{1}{\mathcal{V}}\int w\left(\mathbf{r}\right)\phi\left(\mathbf{r}\right)d\mathbf{r}, \tag{S2}$$

where $\bar{\phi}$ is the mean volume fraction of the brush, $\mathcal{V}$ is the system volume, Q is the partition function per chain, and w is the self-consistent field. Essentially, the first term represents the total free energy of the polymer in the field relative to a uniform fluid state and the second term removes the average internal free energy from the field.[2]

The partition function of a chain with a total number of N segments described by the parameter s going from 0 at the free end and 1 at the tethered end is defined as,

$$Q = \int q(\mathbf{r}, s)q^{\dagger}(\mathbf{r}, s)d\mathbf{r}, \tag{S3}$$

where $q(\mathbf{r}, s)$ is the forward propagator for a chain of sN segments with one end free and the other fixed at $\mathbf{r}$ in space, and $q^{\dagger}(\mathbf{r}, s)$ is the backward propagator for a complementary chain of $(1-s)N$ segments with one end tethered to the surface and the other fixed at $\mathbf{r}$ in space. These two partition functions are determined by solving the modified diffusion equations:

$$\frac{\partial q(\mathbf{r}, s)}{\partial \mathrm{s}} = \left[R_g^2\nabla^2 - w(\mathbf{r})\right]q(\mathbf{r}, s) \tag{S4}$$

and

$$\frac{\partial q^{\dagger}(\mathbf{r}, s)}{\partial \mathrm{s}} = -\left[R_g^2\nabla^2 - w(\mathbf{r})\right]q^{\dagger}(\mathbf{r}, s) \tag{S5}$$

satisfying the boundary conditions $\frac{\partial q}{\partial \mathrm{z}}(-\frac{H}{2}, s) = 0$, $\frac{\partial q}{\partial \mathrm{z}}(\frac{H}{2}, s) = 0$, $\frac{\partial q^{\dagger}}{\partial \mathrm{z}}\left(-\frac{H}{2}, s\right) = 0$, and $\frac{\partial q^{\dagger}}{\partial \mathrm{z}}(\frac{H}{2}, s) = 0$, as well as the initial conditions $q\left(\mathbf{r}, 0\right) = 1$, $q^{\dagger}\left(\mathbf{r}, 1\right) = \delta(z + \frac{H}{2})$ for the lower brush. The volume fraction is then calculated using the partition functions,

$$\phi\left(\mathbf{r}\right) = \frac{\bar{\phi}\mathcal{V}}{Q}\int_0^1 q^{\dagger}(\mathbf{r}, s)q(\mathbf{r}, s)ds. \tag{S6}$$

The configuration of the system corresponds to the one that minimizes eq (S2) subjected to eq (S1).

We generally follow the numerical procedure of ref 3 to solve the modified diffusion equations. Starting with an initial guess of $w(z)$, we employ the Crank-Nicholson method[4] to solve for $q(z,s)$ and $q^{\dagger}(z,s)$. The domain integrals regarding $Q(z)$ and $\phi(z)$ are accomplished by an extended trapezoidal method. We obtain a new field $w^{k+1}(z)$ through a Picard iteration scheme where $\alpha\left[\phi\left(z\right)+\phi\left(-z\right)-1\right]$ with $0<\alpha\leq 1$ is repeatedly added to the old $w^{k}(z)$. The convergence is met until $\left|\phi\left(z\right)+\phi\left(-z\right)-1\right|<0.001$ for $-\frac{H}{2}\leq z\leq\frac{H}{2}$.

References

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