Polymer Brushes Immersed in Two-Component Solvents with Pure Volume Exclusion: Effect of Solvent Molecular Shape

Congcong Li, Tiancai Zhang, Yingzi Yang,* Ping Tang, and Feng Qiu*

The State Key Laboratory of Molecular Engineering of Polymers, Key Laboratory of Computational Physical Sciences, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

ABSTRACT: Polymer brushes have wide application in surface modification. We study dense, short polymer brushes immersed in a mixing solvent under athermal conditions using the classical density functional theory. The brush polymer is short so that the equilibrium behavior of the brush deviates far from the scaling laws for infinite brush chains. The excluded volume interaction is the only interaction in the system. We compare the excluded volume effect of solvent molecules of different shapes. Two types of mixing solvents are considered: solvent composed of linear oligomers and monomers, or that of spherical particles and monomers. The effects of grafting density, solvent molecular size, and solvent number density on the brush height, the density profiles, the relative excess adsorption, and the brush–solvent interface width are systematically analyzed. In the adsorption aspect, the spherical particles have stronger ability than the linear oligomers do to penetrate through the brush layer and gather at the substrate. In the screening aspect, the oligomers are more capable of screening the excluded volume interaction between the brush chains than the spherical particles. The brush–solvent interface width decreases monotonically with increasing oligomer length, but it has a minimum with the increasing spherical particle size. Our research differentiates the attractive-interaction-induced phenomenon and the volume-exclusion-induced phenomenon in dense brush systems and exhibits the difference in the antifouling properties of the brushes contacting solvent molecules of different shapes.

I. INTRODUCTION

Polymer brushes are polymer chains with one end covalently grafted to a surface. The density of the grafting points is high so that the polymer chains stretch strongly away from the grafting substrate. Polymer brushes are central models in many important problems in polymer science, such as polymeric surfactants and structures formed by block copolymers. One of the early applications of polymer brushes was to cover the surface of colloidal particles to effectively avoid the flocculation of the particles and thus promote the stability of the colloidal systems. Now polymer brushes have become a significant focus of polymer research with the demand for straightforward and versatile surface modification (adsorption, wetting, and lubrication), and with their use in biology-relevant applications including resistance to nonspecific binding, cell bioadhesion, thermostresponsive surfaces, targeted protein binding, etc.

In experiments, polymer brushes can be synthesized according to two basic strategies, named as the “grafting to” and the “grafting from” techniques. The “grafting to” method refers to binding end-functionalized polymer molecules to an appropriate substrate to form polymer brushes. The “grafting from” method means preparing a surface with immobilized initiators followed by polymerization. The latter one is more promising in the synthesis of polymer brushes with high grafting density. With controlled grafting density and polymerization, the physical properties of the brushes are investigated in the experiments, including the swelling behavior, order–disorder transition, brush height, interface roughness, nanopatterns with selective solvents, etc.

The theory for polymer brushes has been developed for more than 40 years. The first scaling description of the chain configurations and interactions of polymer brushes was given by Alexander in 1977. The latter one is more promising in the synthesis of polymer brushes with high grafting density. With controlled grafting density and polymerization, the physical properties of the brushes are investigated in the experiments, including the swelling behavior, order–disorder transition, brush height, interface roughness, nanopatterns with selective solvents, etc.

The theory for polymer brushes has been developed for more than 40 years. The first scaling description of the chain configurations and interactions of polymer brushes was given by Alexander in 1977. Then, the scaling theory for the brushes was developed. The scaling theory was based on the model that all chains are divided into “blobs” of the size related to the grafting site distance and the geometry of the grafting substrate. It employed the assumption that the density...
profile of a flat brush is essentially uniform except for the two adjustment regions at the end (i.e., the grafting end at the substrate and the free end near the upper layer of the brush). However, assuming the strong-stretching conformation and infinite chain length, Milner et al elucidated the existence of a parabolic profile of segment density distribution.\(^{17}\) Moreover, mean field theory approaches,\(^{17–20}\) molecular dynamics (MD) simulations,\(^{21}\) and Monte Carlo (MC) simulations\(^{22}\) all predicted that the free end segment can distribute over a wide region in the whole brush layer rather than in a narrow upper layer. Despite the detail difference originated from model settings, all of the theories and simulations emphasize that the conformation of brush chains is very different from that of the typical flexible chains immersed in solution. With the high grafting density, the brush polymers stretch along the normal direction to the surface due to the excluded volume interaction.\(^{1} \) Therefore, the classical density functional theory (DFT), which can employ full volume exclusion interactions,\(^{17} \) has been widely used to study the thermal equilibrium behaviors of the dense, short polymer brushes in the past two decades.\(^{23,24,26–29} \) The DFT calculations are proved to have excellent agreement with MC and MD simulations in many systems, including bi-sphere fluids,\(^{30} \) polymer melts,\(^{31} \) polymeric brushes,\(^{32–34} \) etc.

When polymer brushes are immersed in a solvent, the solvent properties have a great influence on the conformation of brush chains.\(^{5} \) The brushes transform from wet ones to dry ones as the polymerization of the polymeric solvent increases. The crossover is driven purely by entropic effects and is interpreted on the basis of the conformation of the polymeric solvent molecules in the vicinity of the brush.\(^{35} \) The effective anti-fouling surface can be accomplished by a good balance between the brush chain length and the grafting density.\(^{36} \) In the constant pressure MD simulation, with the solvent–brush interaction widely varying with temperature, the brush height changes very little while the monomer density profiles change significantly.\(^{37} \) For the binary mixed brush composed of short and long polymer chains, in addition to the grafting density and the length difference between the chains, the solvent selectivity affects the transition chain length to switching the component in the brush surface outer layer.\(^{38} \) In diblock-copolymer brush systems, when the solvent is poor for both components, the solvophobic interactions drive the chains to self-assemble into micelles having an “onionlike” structure.\(^{39} \)

This paper, we study the dense, short-chain brushes in contact with a two-component fluid composed of oligomers/monomers or spheres/monomers under athermal conditions. We employ the classical DFT approach.\(^{31,41,42} \) The volume exclusion is the only interaction in our model.

We focus on the dense, short polymer brushes with pure volume exclusion interaction for the reasons listed below: (1) If one’s aim is using the minimal amount of polymer to coat the surface and accomplish the proposed properties, such as surface antifouling and particle-suspension stabilizing, it was suggested to use numerous short chains with a high grafting density and a branched structure rather than few very long, linear ones with a low grafting density.\(^{15,29} \) The shortest attached chain satisfying scaling behavior with a 2% accuracy requires at least 30 bonds.\(^{40} \) When the chain length is about 10 in the DFT calculations, the equilibrium behavior of the brush deviates far from the scaling laws that are most accurate for infinite brush chains. (2) We notice that there are already quite a lot of DFT calculations focusing on the short-chain brush systems with attractive interactions,\(^{24,26–28,36,38} \) while only a few emphasize the effect of the pure excluded volume interaction.\(^{23} \) The attractive interactions make the equilibrium behaviors much more complicated. The simpler system without any attractive interaction can show the effect of volume exclusion more clearly. (3) The shape of solvent molecules has a strong impact on surface adsorption. Due to the excluded-volume-induced entropic effect, the hard wall has the tendency to adsorb hard-sphere solvent particles.\(^{43} \) However, the excess adsorption of free linear chains at the hard surface only exists when the volume fraction of the chains is high enough in the bulk.\(^{33} \) Therefore, by systematically comparing the behaviors of the brushes immersed in oligomers and spherical particles, we can understand the antifouling properties of the brushes to molecules of different shapes.

II. MODEL AND THEORY

The polymeric brush, composed of tangentially connected hard-sphere chains with the first segment tethered on a flat substrate, is in contact with binary solvent mixtures of molecules with different shapes. The brush immersed in the solvent mixture of oligomers and monomers is named as the brush/oligomer/monomer (BOM) system, as illustrated in Figure 1a, and the brush immersed in the mixture of hard spherical particles and monomers is named as the brush/particle/monomer (BPM) system, as illustrated in Figure 1b.

![Figure 1](a) Schematic diagrams of (a) the BOM system, and (b) the BPM system. The red chains are brush polymers tethered on the gray substrate, the blue chains represent the oligomers, the blue large spheres are the spherical particles, and the green spheres are the monomers.

In both BOM and BPM systems, the segment number \( N_b = 10 \) of the brush chain is fixed in our calculation. The diameter of the monomer \( \sigma_m \) is chosen as the unit length \( \sigma \). The segments of the brush and the free oligomers are the same, i.e., \( \sigma_b = \sigma_s = \sigma_m = \sigma \). The substrate is covered by the tethered chains with a grafting number density \( \rho_b,0 \). The number densities of the monomer, oligomer segment, and spherical particle in the fluidic bulk are \( \rho_m,0, \rho_o,0, \) and \( \rho_p,0, \) respectively. We define the dimensionless volume density of monomers, oligomers, and spheres as \( \rho_m,0,\sigma^3, \rho_o,0,\sigma^3, \) and \( \rho_p,0,V_p,\sigma^3, \) respectively, where \( N_b \) is the segment number of oligomer and \( V_p = \sigma_o^3/\sigma^3 \) is the dimensionless volume of spherical particles with the diameter \( \sigma_o \).

We employ the classical DFT developed for polymeric fluids and brushes.\(^{27,28,31} \) First, we present here the DFT for the BOM system. The Helmholtz free energy \( F \) is the function of the segment number densities \( \rho_b(R_b), \rho_o(R_o), \) and \( \rho_m(r) \) of the
brush chain, oligomer, and monomer, respectively. \( \mathbf{R}_b \equiv (r_{b,1}, r_{b,2}, ..., r_{b,N_b}) \) and \( \mathbf{R}_o \equiv (r_{o,1}, r_{o,2}, ..., r_{o,N_o}) \) represent the sets of coordinates of the brush chains and the free oligomer chains, respectively. \( F \) is written in the form of the sum of an ideal gas term \( F_{id}[\rho_b(\mathbf{R}_b), \rho_o(\mathbf{R}_o), \rho_m(\mathbf{r})] \) and an excess term \( F_{ex}[\rho_b(\mathbf{R}_b), \rho_o(\mathbf{R}_o), \rho_m(\mathbf{r})] \). The ideal gas term can be expressed exactly as

\[
\beta F_{id} = \int d\mathbf{R}_b \rho_b(\mathbf{R}_b) \ln \rho_b(\mathbf{R}_b) - 1
\]

\[
+ \beta \int d\mathbf{R}_o \rho_o(\mathbf{R}_o) \ln \rho_o(\mathbf{R}_o) - 1
\]

\[
+ \int d\mathbf{r} \rho_m(\mathbf{r}) \ln \rho_m(\mathbf{r}) - 1
\]

and the excess term can be expressed exactly as

\[
\Omega = F + \int d\mathbf{R}_b \left[ \psi_b(\mathbf{R}_b) - \mu_b \right] \rho_b(\mathbf{R}_b)
\]

\[
+ \int d\mathbf{R}_o \left[ \psi_o(\mathbf{R}_o) - \mu_o \right] \rho_o(\mathbf{R}_o)
\]

\[
+ \int d\mathbf{r} \left[ \psi_m(\mathbf{r}) - \mu_m \right] \rho_m(\mathbf{r})
\]

where \( \mu_b \) and \( \psi_b \) are the chemical potentials of the \( \beta \) component and the external potential exerting on the \( \beta \) component, respectively. Here, \( \psi_a(\mathbf{r}_a) = \sum_{i=1}^{N_a} \psi_a(\mathbf{r}_{a,i}) \) for polymeric components (\( \alpha = b \) or \( o \)), where \( \psi_a(\mathbf{r}_{a,i}) \) is the external potential on individual segments.

By minimizing the grand potential, we obtain a set of Euler–Lagrange equations

\[
\rho_b(\mathbf{R}_b) = \exp \left\{ \beta \mu_b - \psi_b(\mathbf{R}_b) - V_b(\mathbf{R}_b) - \frac{\delta \Omega}{\delta \rho_b(\mathbf{R}_b)} \right\}
\]

\[
\rho_o(\mathbf{R}_o) = \exp \left\{ \beta \mu_o - \psi_o(\mathbf{R}_o) - V_o(\mathbf{R}_o) - \frac{\delta \Omega}{\delta \rho_o(\mathbf{R}_o)} \right\}
\]

\[
\rho_m(\mathbf{r}) = \exp \left\{ \beta \mu_m - \psi_m(\mathbf{r}) - \frac{\delta \Omega}{\delta \rho_m(\mathbf{r})} \right\}
\]

The segment number density of the polymeric molecules is the sum of the number density of the individual segments

\[
\rho_b(\mathbf{r}) = \sum_{i=1}^{N_b} \rho_{b,i}(\mathbf{r}) = \sum_{i=1}^{N_b} \int d\mathbf{R}_b \delta(\mathbf{r} - \mathbf{r}_{b,i}) \rho_b(\mathbf{R}_b)
\]

\[
\rho_o(\mathbf{r}) = \sum_{i=1}^{N_o} \rho_{o,i}(\mathbf{r}) = \sum_{i=1}^{N_o} \int d\mathbf{R}_o \delta(\mathbf{r} - \mathbf{r}_{o,i}) \rho_o(\mathbf{R}_o)
\]

Assuming that the density distribution is uniform in the \( x \) and \( y \) directions parallel to the grafting substrate, we simplify the above equations as

\[
\rho_b(z) = k_b e^{\beta \mu_b} \sum_{i=1}^{N_b} e^{-\beta \psi_b(z)} G(z) G_i(z)
\]

\[
\rho_o(z) = k_o e^{\beta \mu_o} \sum_{i=1}^{N_o} e^{-\beta \psi_o(z)} G(z) G_{o,i}(z)
\]

\[
\rho_m(z) = e^{\beta \mu_m - \psi_m(z) - \beta \psi_m(z)}
\]

Among them, \( k_b \) and \( k_o \) are constant coefficients for normalization, \( G \) is the propagator function of the free chains, and \( G_b \) and \( G_o \) are propagator functions for the grafting chain from the grafted end and the free end, respectively. These propagator functions for the grafting chain are determined from the recurrence relation

\[
G_b(z) = 2\pi \sigma \int dz e^{-\beta \psi_b(z)} \theta(\sigma - lz - z') G_{b,i}(z'), \quad \text{with } i = 3, ..., N_b
\]

\[
G_o(z) = 2\pi \sigma e^{-\beta \psi_o(z/2)} \theta(\sigma - lz/2l)
\]
Table 1. Parameters and Their Value Ranges

| Parameter | Description | Value Range |
|-----------|-------------|-------------|
| $N_b$     | the number of segments in the end-tethered chain | 10 |
| $N_o$     | the number of segments in a free oligomer chain | 2–20 |
| $V_p$     | $=\sigma/\sigma^*$, the dimensionless volume of hard sperical particles | 2–20 |
| $\rho_{b,0}$ | the number of tethered chains on the substrate in the unit of $\sigma^{-3}$ | 0.1–0.4 |
| $\rho_{a,0}$ | the number of free monomers in bulk in the unit of $\sigma^{-3}$ | 0–0.6 |
| $\rho_{o,0}$ | the number of free oligomer segments in bulk in the unit of $\sigma^{-3}$ | 0–0.6 |
| $\rho_{p,0}$ | the number of hard spherical particles in bulk in the unit of $\sigma^{-3}$ | 0–0.6/|V_p|

$G_i(z) = 2\pi\sigma \int dz' e^{-\delta h_i(z)} \theta(\sigma - |z' - z'|)G_i^{i+1}(z')$, with $i = 1, \ldots, N_b - 1$ (19)

$G_i^{N_b}(z) = 1$ (20)

Here, $\theta(z)$ is the Heaviside step function.

Due to the geometry difference between the oligomer and spherical particle, the DFT for the BPM system is slightly different from that for the BOM system. The ideal gas term of the Helmholtz free energy and the grand potential of BPM systems are

$$\beta E_{\text{int}} = \int dR_i \phi_i(R_i) [\ln \rho_i(R_i) - 1]$$
$$+ \beta \int dR_i \phi_i(R_i) V_i(R_i)$$
$$+ \int dr \rho_i(r) [\ln \rho_i(r) - 1]$$
$$+ \int dr \rho_{\text{in}}(r) [\ln \rho_{\text{in}}(r) - 1]$$ (21)

$$\Omega = F + \int dR_i \psi_i(R_i) - \mu \rho_i(R_i)$$
$$+ \int dr \psi_i(r) - \mu \rho_i(r) + \int dr \psi_{\text{in}}(r) - \mu_{\text{in}}(r)$$ (22)

where $\rho_i(r)$ and $\mu_i$ are the number density and chemical potential of particles, respectively. Similarly, we assume the uniformity in the $x$ and $y$ directions

$$\rho_i(z) = e^{\delta h_i(z) - \delta^2 h_i(z)}$$ (23)

In both BOM and BPM systems, the fundamental interaction between the two components is the hard-sphere repulsion

$$v_{a,b} (z) = \begin{cases} +\infty, & z \leq (\sigma_a + \sigma_b)/2 \\ 0, & \text{otherwise} \end{cases}$$ (24)

Here, $\sigma_a, \sigma_b = b, o, p, m$. We employ a hard-wall potential for the interaction between the flat substrate and the components

$$v_{a,\text{sub}} (z) = \begin{cases} +\infty, & z \leq \sigma_a/2 \\ 0, & \text{otherwise} \end{cases}$$ (25)

Therefore, the system has only the volume exclusion interactions and is under athermal conditions.

For clarity, some parameters and their value ranges in our DFT calculation are summarized in Table 1.

With the assumption of uniform densities in $x$ and $y$ directions, we define the brush height as

$$h = 2 \int dz [\rho_b(z)]/\int dz \rho_b(z)$$ (26)

The local volume fraction of the $a$-component is

$$\phi_a(z) = \int dz \rho_a(z)$$ (27)

The adsorption of the competitive components in the mixture solvent is analyzed by the relative excess adsorption quantity $A_i^{\alpha, \beta}$

$$A_i^{\alpha} = \int (\rho_\alpha(z) - \rho_{\alpha,0}) dz$$ (28)

$$\rho_\alpha(z) = \frac{\phi_\alpha(z)}{\phi_b(z) + \phi_m(z)}$$ (29)

$$\rho_{\alpha,0}(z) = \frac{\phi_{\alpha,0}}{\phi_{b,0} + \phi_{m,0}}$$ (30)

here, $\rho_\alpha$ stands for the volume fraction of the $\alpha$ component in the mixed solvent, while $\rho_{\alpha,0}$ is the corresponding value in bulk.

III. RESULTS AND DISCUSSION

The DFT presented above is used to calculate the thermal equilibrium behavior of the short-chain brushes in contact with the two-component fluid (oligomer/monomer fluid or particle/monomer fluid). The volume exclusion interaction, which is described by the hard-sphere potential and the hard-wall potential, is the only interaction in the system.

The self-consistent field theory (SCFT) predicted the absence of distinct scaling regime for brush chains less than 100 monomers, and as indicated by MC simulations, the shortest attached poly(ethylene oxide) chain satisfying the scaling law for an infinite long chain with a 2% accuracy has 30 bonds. Moreover, it is believed that the efficient way to stabilize the particles against flocculation with a minimal amount of polymer is using numerous short brush chains rather than few very long ones. For short chains, the excluded volume effect is more dominant than the conformational entropy. When the grafting density $\rho_{b,0}\sigma^2$ is higher than $N_b^{1/5}$, which is the critical grafting density between the mushroom conformation and the dense brush, the brush chains are stretched along the direction perpendicular to the grafting substrate. Therefore, we fix the brush chain length $N_b = 10$, and only consider the grafting density $\rho_{b,0}\sigma^2 > 0.1$. Within our parameter space, the brush height $h$ increases rapidly with $\rho_{b,0}$. The brush segment density is assumed to be uniform in the directions parallel to the substrate.

The system is under the athermal conditions, where volume exclusion is the only interaction between the components.
besides the bonding potentials in eqs 2 and 3. All of the phenomena observed in this work are attributed to the competition between the excluded-volume-induced entropic effect and the chain conformational entropy.

The total segment density in the solvent bulk in the BOM system is fixed, i.e., \( \rho_0 = \rho_{o,0} + \rho_{m,0} = 0.6/\sigma^3 \). The packing fraction \( \eta = \pi \rho_0 \sigma^2 / 6 \) of the fluidic bulk is 0.314. The corresponding BPM system has the same packing fraction in the bulk, i.e., \( \rho_0 = \rho_{p,0} V_p + \rho_{m,0} = 0.6/\sigma^3 \).

In this paper, we focus on the effect of solvent molecular shape on the brush behaviors. We compare the results in the BOM and BPM systems. We analyze the brush height \( h \), the density profiles, the relative excess adsorption quantities, and the width \( w \) of the brush–solvent interface by varying the grafting density \( \rho_{o,0} \), the bulk densities of the solvents, and the size of the solvents. By comparing our results with previous calculations employing attractive interactions, we are able to distinguish between the excluded-volume-induced phenomenon and the attractive-interaction-induced phenomenon.

III. Brush Height \( h \). With high grafting density, the brush height \( h \) is determined by the competition between several aspects. First, the excluded volume interaction between the tethered polymers forces the chains to stretch perpendicularly to the substrate. Second, the conformational entropy of the brush chain tends to restore the random walking. Third, the solvents generate the osmotic pressure, penetrate into the brush layer, and partially screen the excluded volume interaction between the brush chains. Note that the height of the brush without solvent (\( \rho_{m,0} = \rho_{o,0} = \rho_{p,0} = 0 \)) is always higher than that of the brush immersed in a solvent in our model. The brush height \( h \) varies with the grafting density \( \rho_{o,0} \), the bulk density of the oligomers or spherical particles \( (\rho_{o,0} or \rho_{p,0} V_p) \), and the volume of the oligomers or spherical particle \( (N_o or V_p') \), as shown in Figure 2.

The grafting density \( \rho_{o,0} \) is one of the most significant parameters to the brush behavior. For the dense brushes, the distance between the neighboring grafting sites on the substrate is less than the radius of gyration of a single tethered chain. The chains stretch perpendicularly to the substrate due to the contacting (exclusive) interaction between each other. The higher \( \rho_{o,0} \) causes stronger stretching. Consequently, the brush height \( h \) increases monotonically with \( \rho_{o,0} \) as shown in Figure 2a.

With fixed \( \rho_{o,0} \) and \( N_o \) in BOM systems, \( h \) decreases with increasing \( \rho_{o,0} \), indicating less stretching of the brush chains with the higher oligomer density, as shown in Figure 2b. This is ascribed to the screening effect of the mobile oligomers. The mobile chains screen out the interactions between the grafted chains and consequently decrease the brush thickness. The screening effect is stronger with higher \( \rho_{o,0} \). However, \( h \) in the BPM systems exhibit a more complicated behavior with \( \rho_{p,0} V_p \). With different particle bulk densities, \( h \) can be either increasing or decreasing monotonically with increasing \( \rho_{p,0} V_p \), as shown in Figure 2b.

With moderate grafting density \( (\rho_{o,0} \sigma^2 = 0.1) \), \( h \) in the BOM system decreases smoothly with increasing \( N_o \) and approaches the limit value, as shown in Figure 2c. Although the free oligomers are too short for the brush system to enter the scaling region, this phenomenon agrees with the equilibrium brush behavior predicted by de Gennes that \( h \) decreases with increasing \( N_o \) in the mobile-chain-dominated fluid. However, the scaling law \( N_o^{1/4} \) for infinite long-chain brushes is not valid in our model, because the tethered chain length is too short to produce the accurate scaling law. In the BPM system with \( \rho_{o,0} \sigma^2 = 0.4 \), \( h \) is stable when \( N_o \) varies, as shown in Figure 2c.

In the BPM systems, as shown in Figure 2c, \( h \) increases with \( V_p \) in general, except when \( V_p < 5 \) and \( \rho_{o,0} \) is low. Apparently, \( h \) in the BPM system also approaches a limit value before \( V_p \) reaches the critical size for the phase separation between the hard-sphere particles and hard-sphere monomers.

In conclusion, the brush height \( h \) in both BOM and BPM systems is sensitive to the grafting density \( \rho_{o,0} \). Increasing \( \rho_{o,0} \sigma^2 \) from 0.1 to 0.4 causes the increase of \( h \) for approximately 50%. The solvent component density in bulk \( (\rho_{o,0} + \rho_{p,0} V_p) \) and the solvent volume \( (N_o and V_p) \) only influence \( h \) in a range less than 20% within our parameter space. The brush in the BPM system is always higher than that in the corresponding BOM system with \( N_o = V_p \) \( \rho_{o,0} = \rho_{p,0} V_p \) and the same \( \rho_{o,0} \). The difference between the \( h \) values in the corresponding BOM and BPM systems remains approximately constant with increasing \( \rho_{o,0} \) as shown in Figure 2a. However, the dependence of \( h \) on the solvent component density and the solvent volume is different in the BOM and BPM systems. To understand the phenomenon, we will discuss the segment density distribution of all components in the following part.

III.II. Density Profiles. We assume the uniform density distribution in \( x \) and \( y \) directions parallel to the grafting substrate. Thus, only the density profiles in the \( z \)-direction normal to the flat substrate are analyzed. We differentiate three layers in the brush region according to the density profiles and the solvent adsorption modes. (1) The substrate layer, where the initial segments of the brush stretch strongly. The diffusion of the solvent molecules through the brush to stay in this layer is named primary adsorption. (2) The inner layer, where the brush segment density \( \rho_b(z) \) oscillates around a density plateau. The adsorption of solvent particles in the inner layer is named ternary adsorption. (3) The outer layer, where \( \rho_b(z) \)
decreases and approaches zero. The outer layer is the brush–solvent interface. The solvent adsorption at the brush–solvent interface is named secondary adsorption.

The density profiles with various grafting densities $\rho_{b,0}$ are plotted in Figure 3. The increasing $\rho_{b,0}$ causes the lift of the brush density plateau and the increase of the number of density peaks in the inner layer. Correspondingly, less solvents penetrate into the brush layer with higher $\rho_{b,0}$ in both BOM and BPM systems.

Due to the excluded-volume-induced entropic effect, the excess adsorption on the wall is positive in the system of hard-sphere fluid contacting with a hard wall. Similar excess adsorption was also found in polymer melt contacting with a hard wall when the packing fraction of the polymer in bulk is higher than 0.3. The brush creates a barrier to prevent the oligomers and spherical particles from the substrate. As shown in Figure 3, when $\rho_{b,0}\sigma^2 = 0.1$ and 0.2, both the oligomers and spherical particles overcome the barrier and form the primary...
adsorption layer on the substrate. In particular, with \( \rho_{b,0} \sigma_b^2 = 0.1 \), the peak of spherical particle density distribution \( \rho_s(z) \) on \( z = \sigma_p/2 \) is even higher than the spherical particle density in the bulk, \( \rho_{p,0} \). Therefore, the moderate grafting density \( \rho_{b,0} \sigma_b^2 = 0.1 \) is insufficient to protect the substrate from contacting with the oligomers and spherical particles.

When \( \rho_{b,0} \sigma_b^2 = 0.4 \), as shown in Figure 3, all of the oligomers and spherical particles are squeezed out of the substrate layer and the inner layer of the brush, and only the small solvent can stay in the substrate layer.

The density profiles with fixed \( \rho_{b,0} \) \( N_o \) and various \( \rho_{b,0} \) in the BOM system are shown in Figure 4a. With the high grafting density \( \rho_{b,0} \sigma_b^2 = 0.4 \), increasing \( \rho_{b,0} \) hardly influences the brush segment density distribution \( \rho_b(z) \). In the substrate layer, \( \rho_b(z) \) for \( z < 1 \) decreases slightly with increasing \( \rho_{b,0} \). In the outer layer, \( \rho_b(z) \) for \( z > 4 \) lifts a little in the smaller \( z \) region and decreases slightly in the larger \( z \) region. This indicates the sharpening of the brush–solvent interface with increasing \( \rho_{b,0} \).

In the inner layer, \( \rho_b(z) \) for \( 1 < z < 4 \) hardly changes with \( \rho_{b,0} \) under the high grafting density conditions.

The brush segment density \( \rho_b(z) \) responds more strongly to the solvent bulk density in the BPM system than in the BOM system, as shown in Figure 4b. With increasing \( \rho_{p,0} \), \( \rho_b(z) \) decreases obviously in the substrate layer and the inner layer, while the frontier of the brush moves to larger \( z \). Interestingly, although the brush chain stretches more strongly in the BPM system than in the corresponding BOM system, less monomers are found in the substrate layer and inner layer. We attribute the conformational change of the brush chains in response to \( \rho_{p,0} \) to the variety of osmotic pressure instead of the swelling effect of the monomer. When \( \sigma_p > \sigma_m \) and the total volume fraction of the solvent is fixed, the increasing of \( \rho_{p,0} \) results in the decrease of the total molecular number in the solvent. The osmotic pressure exerted on the brush, which screens the excluded volume interaction between the brush chains, is reduced correspondingly. Consequently, the brush chain stretches more strongly with larger \( \rho_{p,0} \).

Note that, in Figure 4b, the curves of \( \rho_b(z) \) and \( \rho_s(z) \) show the peaks of secondary adsorption in the outer layer of the brush when \( \rho_{p,0} \) is high enough.

The segment density \( \rho_b(z) \) of a very dense brush with \( \rho_{b,0} \sigma_b^2 = 0.4 \) is also hardly influenced by the dimensionless solvent molecular volume \( N_o \) and \( V_p \), as shown in Figure 5. Comparing the BOM and BPM systems, we find that \( \rho_b(z) \) responds to \( V_p \) a bit more strongly than to \( N_o \). As shown in Figure 2c, \( h \) in the BPM system has a visible increase with \( V_p \) when \( \rho_{b,0} \sigma_b^2 = 0.4 \), while \( h \) in the BOM system stays nearly constant with varying \( N_o \).

With the high grafting density \( \rho_{b,0} \sigma_b^2 = 0.4 \), the behaviors of the density distributions of the solvents are different in the BOM and BPM systems, as shown in Figure 5. When \( N_o = V_p = 2 \), both the oligomers and the spherical particles penetrate into the brush. The primary adsorption peak of the spherical particles is much higher than that of the oligomers. When the molecular size is larger than five, both the oligomers and the spherical particles are squeezed out of the brush. The secondary adsorption peak of spherical particle emerges with large \( V_p \). The behavior of the BPM system agrees with the results of DFT calculation on the brush immersed in the binary mixture of hard spheres by Borówko et al.\(^{25} \) They concluded that the big molecules were adsorbed in the outer layer of the brush, whereas the small ones penetrated through the polymer films and gathered at the hard surface.

However, in the BOM system, the secondary adsorption peak of oligomers is not observed within our parameter space in this work. When \( N_o \) is large, we only find a weak adsorption peak of monomers in the outer layer of the brush at \( z \approx 7 \sigma \). Although the brush chains are very short in our model, we still find a crossover from wet brushes (where the oligomers penetrate the brush) to dry ones (where the oligomers are squeezed out) as the oligomer length increases. This phenomenon was also observed in SCFT calculations,\(^ {25} \) and

---

**Figure 5.** Density profiles (a) of the BOM systems with various \( N_o \) and (b) of the BPM systems with various \( V_p \). Parameters are \( \rho_{b,0} \sigma_b^2 = \rho_{p,0} V_p \sigma_p^2 = 0.4 \) and \( \rho_{b,0} \sigma_b^2 = 0.4 \).
was interpreted as a pure entropic effect of the conformation of the polymeric solvent molecules in the vicinity of the brush. In the SCFT calculation, it was observed that only the monomeric solvent would substantially penetrate the brush and that the effect of the polymeric solvent is to compress the brush by osmotic and conformational entropic pressure. We also present the density profiles with varying $N_o$ and $V_p$ when the grafting density $\rho_b,0$ is relatively low, as shown in Figure 6. With $\rho_b,0 = 0.1$ and the solvent volume $N_o$ or $V_p$ increasing, the decreasing density profiles of the oligomers and the spherical particles show the ordinary phenomenon that it is harder for the large molecules to penetrate into the brush than the small ones. As shown in Figure 6a, the brush becomes dense in the substrate layer and the inner layer when $N_o$ increases in the BOM systems. Consequently, the brush height $h$ decreases monotonically with $N_o$, as shown in Figure 2c. However, as shown in Figure 6b, the increase of $V_p$ only strongly influences the brush segment density in the substrate layer in the BPM systems. In the inner layer and the outer layer, $\rho_b(z)$ responds weakly to the change of $V_p$.

In conclusion, the brush segment density $\rho_b(z)$ is very sensitive to the grafting density $\rho_b,0$. When $\rho_b,0$ is moderate, the brush responds to the change of the solvent environment obviously. However, when $\rho_b,0$ is very high, the brush chains hardly respond to the solvent variation. The secondary adsorption of the spherical particles is observed with a large solvent size and high $\rho_p,0 V_p$, while the secondary adsorption of the oligomers never appears in our calculation.

III.III. Relative Excess Adsorption. By calculating the relative excess adsorption quantities $A_o^e$ and $A_p^e$ (defined in eq 28), we compare the oligomer’s and the spherical particle’s ability to penetrate through the brush barrier. The adsorption of the solvent in the brush depends strongly on the size, shape, and bulk density of the solvent molecule. In the case of the dense brush with pure steric interaction, the brush chains occupy the space near the substrate and generate a barrier to prevent the solvents from the substrate. Therefore, the excess adsorption isotherms for the solvents are negative in our model. However, the relative excess adsorption quantity of the monomer $A_m^e$ is positive, because the monomer is smaller than the other solvents. Without attractive interactions, the smaller
molecules can penetrate through the brush more easily than the larger ones. Moreover, we have \( A^c_b = -A^c_m \) in the BOM systems, and \( A^c_b = -A^c_m \) in the BPM systems. A large absolute value of \( A^c_b \) and \( A^c_m \) indicates a strong barrier for the oligomers and spherical particles to diffuse to the substrate. Note that the barrier is originated from the pure excluded volume effect and the entropic effect. The relative excess quantities varying with the system parameters are shown in Figure 7.

Increasing the grafting density \( \rho_{b,0} \) means the increasing amount of obstacles near the substrate and the less free space for solvents to fill in. As shown in Figure 7a, both \( A^c_b \) and \( A^c_m \) decrease rapidly with increasing \( \rho_{b,0} \). We find that \( A^c_b \) and \( A^c_m \) in the corresponding BOM and BPM systems nearly overlap each other when the oligomers and the spherical particles are small or dilute. However, when the oligomers and spherical particles are large and dominant in the solvent, \( A^c_b \) is obviously lower than \( A^c_m \). This indicates a larger barrier to the spherical particles than that to the corresponding oligomers with the same volume.

With \( \rho_{b,0} = 0 \) (or \( \rho_{p,0} = 0 \)) and \( \rho_{b,0} = 0.6 \) (or \( \rho_{p,0} = 0.6 \)), \( A^c_b \) and \( A^c_m \) vanish, because the fluidic bulk is one-component. As shown in Figure 7b, \( A^c_b \) and \( A^c_m \) are concave curves with \( \rho_{b,0} \) and \( \rho_{p,0} \) respectively. In both BOM and BPM systems, the minimum of the concave curve decreases and shifts to higher \( \rho_{b,0} \) or \( \rho_{p,0} \) when the grafting density \( \rho_{b,0} \) increases or the molecular volume \( N_{o,0} \) or \( V_{p,0} \) increases.

The relative excess adsorption quantities decrease monotonically with \( N_o \) or \( V_p \) with fixed \( \rho_{b,0}, \rho_{p,0} \) and \( \rho_{b,0} \) as shown in Figure 7c. With low \( \rho_{b,0} \) or \( \rho_{p,0} \), \( A^c_b \) in the BOM system approximately equals \( A^c_m \) in the corresponding BPM system. Both of \( A^c_b \) and \( A^c_m \) approach their limit values with the increase of their molecular volumes. However, when the oligomers or the spherical particles dominate the fluidic bulk, \( A^c_m \) decreases with increasing \( V_p \) much faster than \( A^c_b \) does with increasing \( N_o \). Therefore, we conclude that the brush excludes the spherical particles much more strongly than the oligomers when \( N_o \) and \( V_p \) are large. When the brush is dense, the oligomers can squeeze into the brush layer and change their conformation to adapt to the crowded environment. However, the brush chains have to adapt the spherical shape when a spherical particle is buried in the brush. The larger spherical particle causes the greater loss of the brush chain conformational entropy. Therefore, the dense brush provides a much stronger barrier to the large spherical particle than to the oligomer with the same volume.

Comparing our results with the DFT calculation of the brush systems with attractive interactions,\(^ {24-25,28} \) we find two main differences listed below.

First, the azeotropic point never appears in our calculation. The azeotropic point is defined as the zero value of the relative excess adsorption quantity with none of the two solvent components vanishing. Increasing the density of one solvent component (correspondingly decreasing the density of the other one) to make the relative excess adsorption quantity passing the adsorption azeotropic point indicates the reverse of the preference of the brush. In the BPM system with attractive interactions,\(^ {24} \) the adsorption azeotropy was frequently observed. However, it never appears in our calculation with pure hard-wall and hard-sphere interactions. Moreover, the azeotropic point also emerges in the BOM system with the Lennard-Jones potential,\(^ {25,28} \) when the attractive interaction between the brush and the oligomers is sufficient and \( N_o \) is larger than a critical value. Therefore, we conclude that only the BOM and BPM systems with attractive interactions can exhibit the adsorption azeotropic point, where the enthalpy competes with the entropic effects originated in volume exclusion.

Second, the relative excess adsorption quantity decreases monotonically with increasing oligomer’s length in our calculation, while it can either increase or decrease with the oligomer’s length in the BPM system with the Lennard-Jones potential.\(^ {28} \) According to Figure 12 in Borówno et al.’s work,\(^ {28} \) when the attractive interaction between the brush and the oligomers is stronger than that between the brush and the monomers, the behavior of the relative excess adsorption in response to the increasing oligomer length is different on two sides of the critical oligomer segment density. In our model, lacking attractive interactions, the behavior of the relative excess adsorption quantity is much simpler. The longer oligomers are always more strongly excluded by the dense brushes than the shorter ones.

III.IV. Width of the Brush-Solvent Interface. As predicted by previous theories and simulations on polymeric brushes,\(^ {16,21,33} \) the brush with high grafting density has a fluidic inner layer with approximately constant density and an outer layer between the brush and solvents with decreasing brush segment density. We analyze the width of the outer layer, i.e., the width of the brush-solvent interface, in the BOM and BPM systems.

As shown in Figures 3−6, the number density of the brush segments \( \rho_b (z) \) oscillates strongly. The volume fraction of the brush segments \( \phi_b (z) \) is much smoother than \( \phi_b (z) \). In the following part, we only focus on the brushes with \( \rho_{b,0} \sigma^2 = 0.4 \), and analyze the interface width \( w \) by fitting \( \phi_b (z) \) with the function \( \phi_b = B/\{1 - \tanh(2/w(z - C))\} \), as shown in Figure 8. Here, \( B \) is the constant volume fraction in the inner layer of the brush, and \( C \) is the center of the interface region. The brush height \( h \) with \( \rho_{b,0} \sigma^2 = 0.4 \) varies between \( 6 \sigma \) and \( 7 \sigma \). The width of the interface analyzed in our short polymer brush systems always occupies more than 30% of the brush layer.

In the BOM systems, the width \( w \) of the brush-solvent interface decreases with increasing \( N_o \) and approaches the convergent value, as shown in Figure 9a. The convergent value decreases with increasing \( \rho_{b,0} \). Although \( w \) varies with \( \rho_{b,0} \) and \( N_o \), the fitting parameters \( B \) and \( C \) hardly change. The volume fraction plateau value is \( 0.36 < B < 0.38 \), and the center position of the interface area is \( 5.75 < C < 5.95 \). We interpret the behavior of \( w \) in the BOM system in the same way as de Gennes did.\(^ {21} \) The mobile chains screen out the interaction between the grafted chains when \( \phi_{b,0} \) dominates \( \phi \) in the bulk, and the brush chains are ideal when the brush contacts with...
the melt of polymer with $N_o$ much greater than $N_v$. This screening effect strengthens with increasing $N_o$ and $\rho_{b,0}$.

The width of the brush–solvent interface $w$ in the BPM systems is shown in Figure 9b. $w$ is nonmonotonic with the molecular volume $V_p$ in the BPM systems. With $\rho_{b,0}\sigma^2 = 0.4$ and fixed $\rho_{b,0}$, $w$ decreases with $V_p$ until it reaches its minimum at $V_p \approx S$, and then increases with $V_p$ to approach a convergent value related to $\rho_{b,0}$. We relate this phenomenon with the density profiles in Figure 5b and interpret as follows. On one hand, the spherical particles distributing in the outer layer of the brush expands the brush–solvent interface. With increasing $V_p$, the ability of the spherical particles to penetrate into the brush weakens, and the ability to expand the interface weakens accordingly. On the other hand, increasing $V_p$ causes the decrease of the osmotic pressure exerted on the brush, because the total molecular number in the bulk decreases with increasing $V_p$. The brush chain stretches more strongly with lower osmotic pressure. Therefore, $w$ increases with decreasing osmotic pressure in the large $V_p$ limit. The competition between these two aspects causes $w$ to decrease with small $V_p$ and increase to approach a convergent value with large $V_p$. In Figure 9b, the minimum of $w$ is at $V_p \approx S$, which occurs in correspondence with the molecular volume with which the primary adsorption fades. Note that $B$ and $C$ change more strongly in the BPM systems. For example, with $\rho_{b,0}V_p\sigma^2 = 0.5$ and $\rho_{b,0}\sigma^2 = 0.4$ in Figure 9b, $B$ decreases from 0.36 to 0.33 and $C$ increases from 5.98 to 6.53, when $V_p$ increases from 2 to 20.

**IV. CONCLUSIONS**

We have studied the equilibrium behaviors of the short polymer brushes immersed in a two-component solvent under athermal conditions, via using the classical DFT. The brush chains are very short so that the equilibrium behavior of the brush deviates far from the scaling laws that are most accurate for infinite brush chains. The interaction in our model is pure volume exclusion. We employ the hard-sphere interactions between different components and the hard-wall interactions between the substrate and the components. We focus on the brush height $h$, the density profiles, the relative excess adsorption quantities, and the width $w$ of the brush–solvent interface. We compare the results in the BOM and BPM systems to reveal the different volume exclusion effects of the linear oligomers and the spherical particles to the brushes.

In both BOM and BPM systems, the brush height $h$ increases strongly with the grafting density $\rho_{b,0}$. The oligomers have a stronger ability to screen the excluded volume interaction between the brush chains. Therefore, the brush height $h$ in the BOM system is always lower than that in the corresponding BPM system with the same solvent molecule volume and density ($\rho_{p,0}V_p = \rho_{o,0}$). In the BOM system, $h$ decreases monotonically with the oligomer density $\rho_{o,0}$ in the bulk. However, $h$ can either increase or decrease with increasing $\rho_{p,0}$ depending on the volume of the spherical particles in the BPM system.

The spherical particles exhibit stronger primary adsorption on the substrate than the oligomers. The secondary adsorption in the outer layer of the brush is observed in the BPM systems when $V_p$ is large enough. However, the secondary adsorption of the oligomers is not observed in the BOM systems with the parameter space employed in this paper.

The negative value of the relative excess adsorption quantities, $A_e^o$ and $A_e^p$, indicates that both the oligomers and spherical particles are more excluded by the brush than the monomers. When the molecular volume is large, $A_e^o$ in the BOM systems is obviously higher than $A_e^p$ in the corresponding BPM systems.

With very high grafting density of the brush ($\rho_{b,0}\sigma^2 = 0.4$), the brush–solvent interfacial width $w$ decreases with oligomer length $N_o$ monotonically in the BOM systems, while it has a minimum with increasing $V_p$ in the BPM systems.

We would like to emphasize that the equilibrium behavior in our model is determined by the competition between the excluded volume interaction, the translational entropy, and the conformational entropy. Our simple model helps to reveal the pure volume exclusion effects, therefore the phenomena strongly depending on the attractive interactions, such as the azeotropic points and the alternative adsorption behavior with various molecular size, do not exist in our model.

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: yang_yingzi@fudan.edu.cn (Y.Y.).
*E-mail: fengqiu@fudan.edu.cn (F.Q.).

**ORCID**

Yingzi Yang: 0000-0002-8514-8228
Ping Tang: 0000-0003-0253-1836

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 21774026) and the Ministry of Science and Technology of the People’s Republic of China (Grant No. 2016YFA0203301).
REFERENCES

(1) Milner, S. T. Polymer Brushes. Science 1991, 251, 905–914.
(2) Milner, S. T.; Witten, T. A.; Cates, M. E. Theory of the Grafted Polymer Brush. Macromolecules 1988, 21, 2610–2619.
(3) Currie, E. P. K.; Norde, W.; Cohen Stuart, M. A. Tethered polymer chains: surface chemistry and their impact on colloidal and surface properties. Adv. Colloid Interface Sci. 2003, 100-102, 205–265.
(4) Chen, W.-L.; Cordero, R.; Tran, H.; Ober, C. K. 50th Anniversary Perspective: Polymer Brushes: Novel Surfaces for Future Materials. Macromolecules 2017, 50, 4089–4113.
(5) Olivier, A.; Meyer, F.; Raquez, J.-M.; Damman, P.; Dubois, P. Surface-initiated controlled polymerization as a convenient method for designing functional polymer brushes: From self-assembled monolayers to patterned surfaces. Prog. Polym. Sci. 2012, 37, 157–181.
(6) Prucker, O.; Rühe, J. Synthesis of Poly(styrene) Monolayers Attached to High Surface Area Silica Gels through Self-Assembled Monolayers of Azido Initiators. Macromolecules 1998, 31, 592–601.
(7) Zhao, B.; Brittain, W. J. Polymer brushes: surface-immobilized macromolecules. Prog. Polym. Sci. 2000, 25, 677–710.
(8) Sanjuan, S.; Perrin, P.; Pantoustier, N.; Tran, Y. Synthesis and Swelling Behavior of pH-Responsive Polybase Brushes. Langmuir 2007, 23, 5767–5778.
(9) Maher, M. J.; Jones, S. D.; Zografas, A.; Xu, J.; Schibur, H. J.; Bates, F. S. The Order-Disorder Transition in Graft Block Copolymers. Macromolecules 2018, 51, 232–241.
(10) Habicht, J.; Schmidt, M.; Rühe, J.; Johannsmann, D. Swelling of Thick Polymer Brushes Investigated with Ellipsometry. Langmuir 1999, 15, 2460–2465.
(11) Dukes, D.; Li, Y.; Lewis, S.; Benewicz, B.; Schadler, L.; Kumar, S. K. Conformational Transitions of Spherical Polymer Brushes: Synthesis, Characterization, and Theory. Macromolecules 2010, 43, 1564–1570.
(12) Zhao, W.; Krausch, G.; Rafailovich, M. H.; Sokolov, J. Lateral Structure of a Grafted Polymer Layer in a Poor Solvent. Macromolecules 1994, 27, 2933–2935.
(13) Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. Nanopattern Formation from Tethered PS-b-PDMA Brushes upon Treatment with Selective Solvents. J. Am. Chem. Soc. 2000, 122, 2407–2408.
(14) Alexander, S. Adsorption of Chain Molecules with a Polar Head a Scaling Description. J. Phys. 1977, 38, 983–987.
(15) Witten, T. A.; Pincus, P. A. Colloid Stabilization by Long Grafted Polymers. Macromolecules 1986, 19, 2509–2513.
(16) de Gennes, P. G. Conformations of Polymers Attached to an Interface. Macromolecules 1980, 13, 1069–1075.
(17) Milner, S. T.; Witten, T. A.; Cates, M. E. A Parabolic Density Profile for Grafted Polymers. Europhys. Lett. 1988, 5, 413–418.
(18) Zhulina, E. B.; Borisov, O. V.; Brambacher, L. Theory of a Planar Grafted Chain Layer Immersed in a Solution of Mobile Polymer. Macromolecules 1991, 24, 4679–4690.
(19) Carignano, M. A.; Szleifer, I. Statistical thermodynamic theory of grafted polymeric layers. J. Chem. Phys. 1993, 98, 5006–5018.
(20) Borukhov, I.; Leibler, L. Enthalpic Stabilization of Brush-Coated Particles in a Polymer Melt. Macromolecules 2002, 35, 5171–5182.
(21) Murat, M.; Grest, G. S. Structure of a Grafted Polymer Brush: A Molecular Dynamics Simulation. Macromolecules 1989, 22, 4054–4059.
(22) Weinhold, J. D.; Kumar, S. K. Monte Carlo simulations of engrafted polymer matrices under poor solvent conditions. J. Chem. Phys. 1994, 101, 4312–4323.
(23) Borówko, M.; Rząsko, W.; Sokolowski, S.; Staszewski, T. Density functional approach to the adsorption of spherical molecules on a surface modified with attached short chains. J. Chem. Phys. 2007, 126, No. 214703.
(24) Borówko, M.; Sokolowski, S.; Staszewski, T. Adsorption from Binary Solutions on the Polymer-Tethered Surfaces. J. Phys. Chem. B 2012, 116, 3115–3124.
(25) Borówko, M.; Sokolowski, S.; Staszewski, T. Adsorption from Oligomer-Monomer Solutions on the Surfaces Modified with End-Grated Chains. J. Phys. Chem. B 2012, 116, 12842–12849.
(26) Borówko, M.; Sokolowski, S.; Staszewski, T. Adsorption of oligomers on the polymer-tethered surfaces. J. Colloid Interface Sci. 2011, 356, 267–276.
(27) Xu, X. F.; Cao, D. P. Density functional theory for adsorption of colloids on the polymer-tethered surfaces: Effect of polymer chain architecture. J. Chem. Phys. 2009, 130, No. 164901.
(28) Borówko, M.; Sokolowski, S.; Staszewski, T. Terminally Grafted Chain Layers in Oligomer-Monomer Solutions: Predictions from a Density Functional Theory. J. Phys. Chem. B 2013, 117, 10293–10303.
(29) Xu, X. F.; Cao, D. P.; Wu, J. Z. Density functional theory for predicting polymeric forces against surface fouling. Soft Matter 2010, 6, 4631–4646.
(30) Yu, Y.-X.; Wu, J. Z. Structures of hard-sphere fluids from a modified fundamental-measure theory. J. Chem. Phys. 2002, 117, 10156–10164.
(31) Yu, Y.-X.; Wu, J. Z. Density functional theory for inhomogeneous mixtures of polymeric fluids. J. Chem. Phys. 2002, 117, 2568–2576.
(32) Egorov, S. A. Interactions between polymer brushes in solvents of variable quality: A density functional theory study. J. Chem. Phys. 2008, 129, No. 064901.
(33) McCoy, J. D.; Ye, Y.; Curro, J. G. Application of density functional theory to tethered polymer chains: Athermal systems. J. Chem. Phys. 2002, 117, 2975–2986.
(34) Ye, Y.; McCoy, J. D.; Curro, J. G. Application of density functional theory to tethered polymer chains: Effect of intermolecular attractions. J. Chem. Phys. 2003, 119, 555–564.
(35) Martin, J. I.; Wang, Z.-G. Polymer Brushes: Scaling, Compression Forces, Interbrush Penetration, and Solvent Size Effects. J. Phys. Chem. B 1995, 99, 2833–2844.
(36) Lima, E. R. A.; Jiang, T.; Wu, J. Z. A theoretical study of colloidal forces near amphiphilic polymer brushes. Colloids Surf., A 2011, 384, 115–120.
(37) Grest, G. S. Grafted Polymer Brushes: A Constant Surface Pressure Molecular Dynamics Simulation. Macromolecules 1994, 27, 418–426.
(38) Gong, K.;il; Chapman, W. G. Solvent response of mixed polymer brushes. J. Chem. Phys. 2011, 135, No. 214901.
(39) Zhulina, E. B.; Singh, C.; Balazs, A. C. Forming Patterned Films with Tethered Diblock Copolymers. Macromolecules 1996, 29, 6338–6348.
(40) Sarmoria, C.; Blankschtein, D. Conformational Characteristics of Short Poly(ethylene oxide) Chains Terminally Attached to a Wall and Free in Aqueous Solution. J. Phys. Chem. B 1992, 96, 1978–1983.
(41) Chen, C. Y.; Tang, P.; Qiu, F.; Shi, A. C. Excluded volume effects in compressed polymer brushes: A density functional theory. J. Chem. Phys. 2015, 142, No. 124904.
(42) Chen, C. Y.; Tang, P.; Qiu, F.; Shi, A. C. Density Functional Study for Homodendrimers and Amphiphilic Dendrimers. J. Phys. Chem. B 2016, 120, 5553–5563.
(43) Henderson, D. Fundamentals of Inhomogeneous Fluids; Dekker: New York, 1992.
(44) Biben, T.; Hansen, J.-P. Phase Separation of Asymmetric Binary Hard-Sphere Fluids. Phys. Rev. Lett. 1991, 66, 2215–2218.