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Theoretical Study of Cooperativity in Multivalent Polymers for Colloidal Stabilization

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Multivalent polymers, i.e., copolymers with multiple binding sites, have been proposed recently for stabilization of fusogentic liposomes and other liposomal colloids useful for drug delivery. The performance of such polymers critically depends on their molecular architecture, in particular the strength and frequency of surface anchoring sites along the backbone of a highly soluble polymer. In this work, we investigate the adsorption and surface forces due to multivalent polymers based on coarse-grained polymer models. We find that for W-type polymers that form dangling tails when all anchoring segments are attached to a surface, increasing the chain length at fixed polymer composition leads to a stronger repulsive barrier in the polymer-mediated surface forces thereby increasing the ability of the polymer to stabilize colloidal particles. This prediction conforms to an earlier experiment indicating that increasing the number of hydrophobic anchors along poly(ethylene glycol) polymers results in the cooperative behavior for both surface adsorption and steric stabilization. For M-type multivalent polymers that have weakly anchoring sites placed at the ends, however, addition of binding sites at fixed polymer composition could lead to negative cooperativity, i.e., the more binding sites, the less the amount of adsorption or the weaker the ability of surface protection. The theory also predicts that polymers with two anchoring sites (e.g., telechelic copolymers) are most efficient for colloidal stabilization.

1. Introduction

Attachment of highly soluble polymers onto a solid surface provides an efficient means to minimize often undesirable, nonspecific surface adsorption and to stabilize colloidal particles in a solution. The concept of steric stabilization has been well established and is supported by numerous theoretical and experimental investigations. For instance, β-casein, a flexible protein predominantly consisting of hydrophilic amino acid residues, is broadly used for stabilization of food colloids including dairy-based, oil-in-water emulsions.[1,2] Another well-documented example is the use of hydrophilic polymers such as poly-(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) for improving the biocompatibility of implanted medical devices and for stabilizing liposomes devised as drug carriers.[3,4] It has been demonstrated that incorporation of PEG-derived phospholipids into liposomes drastically prolongs the liposome circulation time in blood, thereby improving the therapeutic efficacy of encapsulated anticancer drugs.[5]

Following a concept originally proposed by Whitesides,[6] Prud'homme and co-workers recently demonstrated that multivalent polymers provide a cooperative mechanism for stabilization of liposomes and other colloidal particles.[7−11] It was conjectured that, in comparison to polymers with single binding site per chain, polymers with multiple binding sites (i.e., multivalency) can lead to a stronger overall surface absorption thus a higher level of surface protection even when the binding energy for each site is relatively weak. In other words, long polymers with multiple binding sites are more efficient than short polymers with only a single binding site at the same composition. The cooperative behavior of multivalent polymers for liposome protection has been proved experimentally by using hydrophobically modified polymers (hm-polymers), such as those obtained by introduction of equally spaced C18 stearylamide hydrophobes into otherwise linear poly(ethylene glycol) (PEG) chains.[7] These comb-graft copolymers provide a protection layer at the liposome surface by cooperative formation of looplike PEG structures. The comb copolymers used by Prud'homme and co-workers are different from those consisting of a charged backbone and hydrophilic side chains that have been successfully used to stabilize red blood cells from lectin-induced hemagglutination and fibroblasts from adhesion to fibronectin-coated surfaces.[12−14]

From the outset, theoretical investigations on steric stabilization have been focused on permanently tethered polymers in a good solvent.[15−18] Polymer brushes of high molecular weight and high tethering density have been

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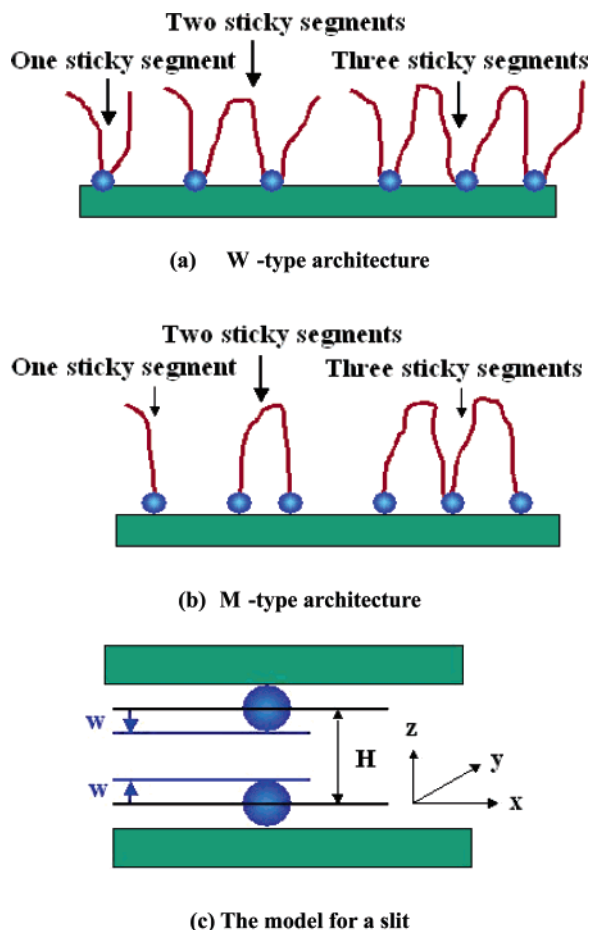(18) Szleifer, I. *Biophys. J.* **1997,** *72,* 595.

Figure 1. Schematics of W- and M-type multivalent polymers (a, b) and the definitions of the slit width and range of the surface potential (c).

recommended for efficient surface protection and for colloidal stabilization. From an experimental viewpoint, however, attachment of long, highly soluble polymers onto a surface is technically difficult because at a fixed surface energy, the increase of chain length means more partitioning of polymers into the bulk solution and eventually leads to the loss of surface protection. For this reason, practical applications are often limited to hydrophilic polymers with moderate molecular weight or chain length. The optimal performance is achieved by a subtle balance of the steric repulsion arising from the immobilized highly soluble polymers and the strength of surface binding. The surface attraction is often provided by the physical adsorption of copolymerized functional groups.

For colloidal stabilization, the surface force introduced by multivalent polymers depends on the polymer−surface interactions as well as polymer architecture. Toward a better understanding of the corporative behavior, this work employs a density-functional theory to examine the effects of polymer architecture, chain length, and anchoring frequency on surface adsorption, solvation forces, and local microscopic structures. We have demonstrated in our previous publications[19,20] that the density-functional theory is able to quantitatively reproduce the simulation results for the structure and thermodynamic properties of polymers and copolymers in the bulk as well as under confinement. The focus of this work is to study, we believe for the first time, the cooperative behavior of multivalent polymers for colloidal stabilization using a theoretical

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approach. Because we lack simulation or experimental data for direct comparison of the theoretical predictions for the microscopic structure and surfaces forces, no effort has been made to match the coarse-grained models to any realistic systems by optimizing the underlying parameters. However, we expect that the results reported in this work retain the qualitative behavior of the cooperativity in multivalent polymers for surface protection and colloidal stabilization.

2. Molecular Models

The objective of this work is to study the cooperative behavior of multivalent polymers in adsorption and surface forces. We consider a minimalist model where each polymer molecule is represented by tangent hard-sphere chains consisting of neutral and surface-binding beads of equal size. Schematically, Figure 1, panels a and b, depicts two types of multivalent polymers considered in this work. The W-type polymers have the surface binding (sticky) segments embedded in the middle of the polymer chain; they are characterized by tails and loops when all the sticky segments are bound to a surface. The M-type multivalent polymers have the sticky segments placed on the ends so that they do not form dangling tails when all the binding segments are adsorbed. Whereas our model is not necessarily representing the hydrophobically modified poly(ethylene glycol) (hm-PEGs) copolymers used in the experiments,[7] each chain retains multiply attachable sites (multivalency) that may exhibit the cooperative behavior.

We assume that in the absence of the sticky segments, the polymers would be in a good solvent. The pair interaction between surface binding segments, denoted by A, are described by a square-well potential:[20]

$$\varphi_{AA}(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon_{AA} & \sigma \leq r \leq \gamma\sigma \\ 0 & r > \gamma\sigma \end{cases} \tag{1}$$

where σ is the segmental diameter and $\gamma\sigma$ is the square-well width. The width and energy parameters are fixed at $\gamma = 1.2$ and $\epsilon_{AA} = 1\,kT$, mimicking the solvent-mediated attraction between the surface-binding segments. Both the pair interaction between neutral segments, denoted by B, and that between a sticky and a neutral segment are described by the hard-sphere potential.

The cooperativity of the surface binding segments is examined by considering the adsorption of the polymers onto a structureless surface and the polymer-mediated surface forces. The surface energy for each sticky segment is also represented by a square-well potential

$$\varphi_{AW}^{att}(z) = \begin{cases} \infty & z < 0 \\ -\epsilon_{AW} & 0 \leq z < w \\ 0 & \text{otherwise} \end{cases} \tag{2}$$

where z indicates the perpendicular distance, w stands for the range of the surface attraction, and ϵ_{AW} denotes the strength of the attractive energy. While the range of the surface attraction is fixed at $w = 0.5\sigma$ in all cases, two values of surface energies are considered, $\epsilon_{AW} = 30$ or 5 kT, corresponding to multivalent polymers with strong or weak binding sites, respectively. Here k represents the Boltzmann constant and T is the absolute temperature. The interaction between a neutral segment and the surface is represented by the hard-sphere potential, i.e., $\epsilon_{BW} = 0$. Figure 1c depicts the definitions of the surface width parameter (w) and the surface separation (H). For all cases,

the polymer volume fraction in the bulk is fixed at $\phi_b = 0.05$. This bulk volume fraction is used only as a reference. A small value is assumed because in practical applications, an ideal situation is that only a small amount of the multivalent polymer leaks into the bulk solution. Nevertheless, we consider the full interactions among segments in the equation of state for the bulk fluid.

3. Density-Functional Theory

A. Helmholtz-Energy Functional. The polymer density functional theory used in this work has been reported in our previous publications.[20−23] Therefore, we recap only the key equations. For a liquid solution containing copolymers of A- and B-type segments, the Helmholtz-energy functional $F[\rho_M(\mathbf{R})]$ can be expressed in terms of an ideal-chain contribution and an excess part that takes into account the nonbonded interactions between segments including the hard-sphere repulsion, correlations due to the chain connectivity, and the short-ranged van der Waals attractions

$$F[\rho_M(\mathbf{R})] = F_{id}[\rho_M(\mathbf{R})] + F_{ex}[\rho_M(\mathbf{R})] \qquad (5)$$

The configurational density $\rho_M(\mathbf{R})$ is defined as a local density in a multidimensional space specified by the positions of all M segments in a polymer chain, $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2 \cdots, \mathbf{r}_M)$. $\rho_M(\mathbf{R})$ is related to the number densities of segments, $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$, by

$$\rho_A(\mathbf{r}) = \sum_{i \in A} \rho_i(\mathbf{r}) = \sum_{i \in A} \int d\mathbf{R} \, \delta(\mathbf{r} - \mathbf{r}_i) \rho_M(\mathbf{R}) \quad (6a)$$

$$\rho_B(\mathbf{r}) = \sum_{i \in B} \rho_i(\mathbf{r}) = \sum_{i \in B} \int d\mathbf{R} \, \delta(\mathbf{r} - \mathbf{r}_i) \rho_M(\mathbf{R}) \quad (6b)$$

In eq 5, the ideal and excess contributions to the Helmholtz energy are, respectively[20]

$$\beta F_{id}[\rho_M(\mathbf{R})] = \int d\mathbf{R} \, \rho_M(\mathbf{R})[\ln \rho_M(\mathbf{R}) - 1] +$$
$$\beta \int d\mathbf{R} \, \rho_M(\mathbf{R}) V_B(\mathbf{R}) \quad (7)$$

$$\beta F_{ex}[\rho_i(\mathbf{r})] = \int d\mathbf{r} \, \{\phi^{hs}[n_a(\mathbf{r})] + \phi^{Chain}[n_a(\mathbf{r})]\} +$$
$$\beta F_{ex}^{att}[\rho_i(\mathbf{r})] \quad (8)$$

where $\beta = 1/kT$, $V_B(\mathbf{R})$ stands for the total bond potential, $\phi^{hs}[n_\alpha(\mathbf{r})]$ and $\phi^{Chain}[n_\alpha(\mathbf{r})]$ are the excess Helmholtz-energy densities due to the hard-sphere repulsion and chain connectivity, respectively, and $\beta F_{ex}^{att}[\rho_i(\mathbf{r})]$ is the reduced excess Helmholtz energy due to van der Waals interactions. The weighted densities $n_\alpha(\mathbf{r})$, $\alpha = 0, 1, 2, 3, V_1, V_2$ are given by[24]

$$n_\alpha(\mathbf{r}) = \sum_j n_\alpha j(\mathbf{r}) = \sum_j \int \rho_j(\mathbf{r}') \omega_j^\alpha(\mathbf{r} - \mathbf{r}') \, d\mathbf{r}' \quad (9)$$

where $\omega_j^\alpha (\alpha = 0,1,2,3,V_1,V_2)$ are weight functions.[24] The expressions for the excess Helmholtz energies and the weight functions can be found in our earlier publications.[20−22] At thermodynamic equilibrium, minimization of the Helmholtz energy yields a variational equation for the configurational density profiles and from which both
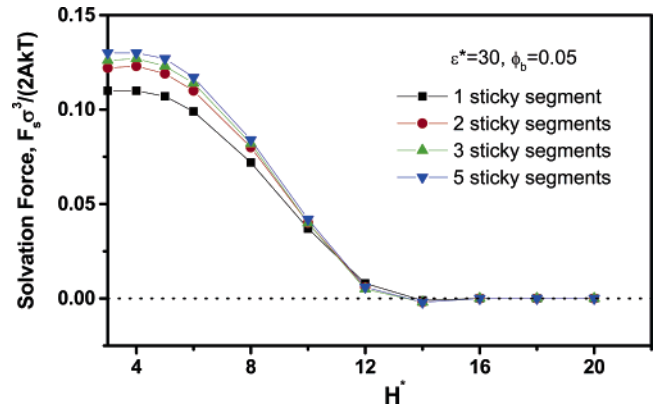
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Figure 2. Solvation forces due to W-type multivalent polymers with a fixed ratio of the numbers of the neutral and sticky segments. Each neutral block consists of 20 segments.

the structure and thermodynamic properties of the system can be calculated.

B. Solvation Forces. The force between two planar surfaces immersed in a multivalent polymer solution is calculated from[25]

$$F_H/(2AkT) = \sum_{j=A,B} \int dz \, \rho_j(z) \frac{\partial \beta \varphi_{jW}}{\partial z} \quad (10)$$

where F_H/A represents the force per unit area on a single surface, a factor of 2 accounts for the fact that the force is exerted to both surfaces, and φ_{jW} is the external potential exerted on segment j. At a given separation, the reduced solvation force per unit area is defined as[19,26]

$$F_s \sigma^3/(2AkT) = (F_H - F_\infty)\sigma^3/(2AkT) \quad (11)$$

where F_∞/A is the force per unit area when the two surfaces are infinitely apart. Equation 11 conforms with the convention that the solvation force disappears at infinite separation.

4. Results and Discussion

We first consider adsorption and solvation forces due to multivalent polymers with strongly binding segments; that is, the surface energy for each sticky segment is 30 kT. Figure 2 shows the reduced solvation forces between two planar surfaces immersed in a dilute solution of W-type multivalent polymers. As mentioned earlier, the polymer volume fraction in the bulk is fixed at $\phi_b = 0.05$. Four types of polymers have been considered, with 1, 2, 3, and 5 binding sites per chain, respectively; the number of neutral segments between two nearest binding sites is equal to 20. At fixed polymer concentration, the total number of segments for each polymer is proportional to the number of binding sites; that is, the corresponding chain lengths are M = 21, 42, 63, and 105, respectively. As expected, we find that the solvation force is essentially everywhere repulsive and declines monotonically with the surface separation, similar to the steric interactions due to polymer brushes or telechelic polymers.[27] The shallow attractive minimum, which occurred at approximately twice the polymer-layer thickness or four times the radius of gyration of the neutral block, is attributed to the bridging effect or the weakly correlated thermal fluctuations of segment densities near the edge of the two adsorbed

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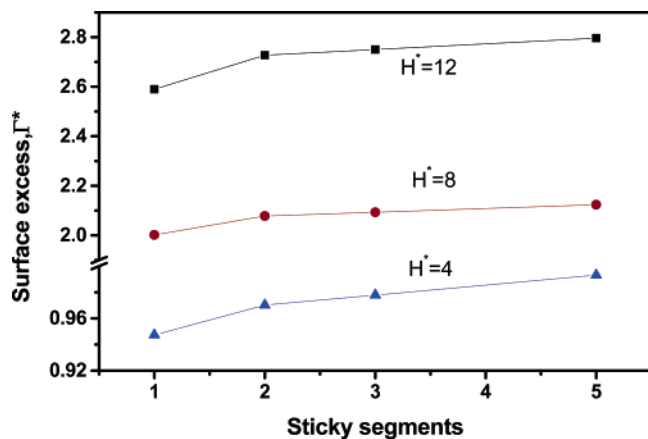(27) Meng, X. X.; Russel, W. B. *Macromolecules* **2003**, *36*, 10112.

Figure 3. Surface excess versus the number of sticky segments for those polymers shown in Figure 2.

polymer layers. Because the neutral blocks have the same size, the thickness of the adsorption layer is essentially independent of the polymer chain length or the number of neutral blocks. However, at the same polymer volume fraction and adsorption energy, the surface force increases with the number of sticky segment monotonically, suggesting a cooperative effect in multivalent polymers for surface stabilization. Such cooperative effect becomes most perceptible for polymers with two surface binding segments and quickly levels off as the number of binding segments is further increased.

The cooperativity of the binding segments is also reflected in the amount of surface adsorption as depicted in Figure 3. At a given separation between the two surfaces, the reduced surface excess, defined as

$$\Gamma^* = \int_0^H (\rho(z) - \rho_b)\sigma^2 \, dz \qquad (12)$$

increases with the number of binding segments monotonically. Similar cooperative behavior was observed in experiments.[7] Although the total amount of adsorption falls monotonically with the surface separation, it is worth noting that the average polymer density at $H^* = 8$ is higher than that either at $H^* = 12$ or at $H^* = 4$. The maximum average density occurs at an intermediate separation because a small separation prohibits the entering of polymer chains due to the size effect while at large separations, there is little surface interaction.

The molecular architecture of multivalent polymers is expected to play an important role in the adsorption behavior and in the polymer-mediated surface forces.[28] To illustrate this point, we consider again the multivalent polymers with 1, 2, 3, and 5 binding sites but with the binding segments placed at the ends. In this case, the polymers form only "loop" like structure when all of the binding sites are attached to a surface. To keep the surface thickness approximately identical, the polymer with only one binding site has 10 neutral segments and all others have 20 neutral segments between two nearest binding sites. Figure 4 presents the solvation forces introduced by the M-type multivalent polymers at conditions the same as those used for W-type copolymers as shown in Figure 2. Although the force profiles due to the W and M types of copolymers are rather similar, the dependence of the solvation force on the number of binding segments or chain length is entirely different. For M-type polymers, cooperativity shows only for those with two sticky segments; that is, the solvation force due to the telechelic polymers
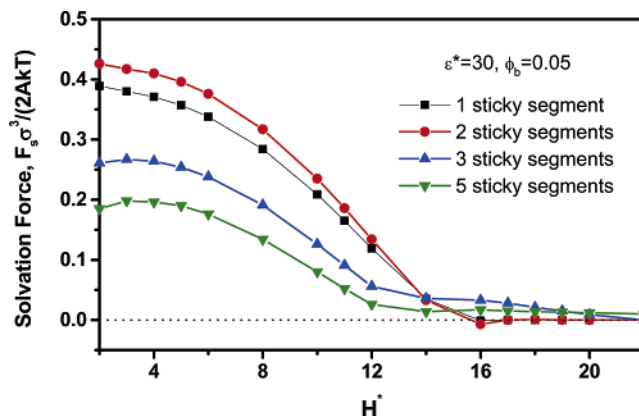
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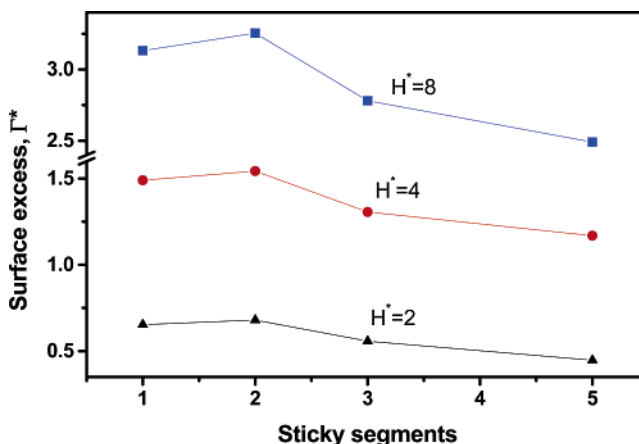**Figure 4.** Solvation forces due to M-type multivalent polymers.

Figure 5. Surface excess versus the number of sticky segments for those polymers shown in Figure 4.

is stronger than those due to polymers with one or multiple binding sites. A direct comparison of Figures 2 and 4 reveals that for all cases, the magnitude of repulsion due to M-type multivalent polymers is much stronger than that due to the W-type polymers. Figure 5 depicts the corresponding adsorption behavior for M-type multivalent polymers with different number of sticky segments. As for W-type multivalent polymers, the strength of repulsion due to M-type multivalent polymers is well correlated with the excess amount of adsorption on the surface; that is, the more excess amount of adsorption, the stronger the surface repulsion.

As discussed earlier, the performance of multivalent polymers for surface protection reflects a subtle balance of the tethering energy and the molecular weight of highly soluble polymer blocks, in particular when the surface energy is relatively weak. To address this point, we have also investigated the solvation forces due to multivalent polymers with weakly binding sites by setting the surface energy for each sticky segment to 5 kT instead of 30 kT. Figure 6 shows the solvation forces due to M-type multivalent polymers with two, three, and seven binding sites at a polymer volume fraction in bulk the same as that considered earlier. At the fixed length of the neutral polymer blocks, the solvation force varies from weakly repulsive for those with two sticky segments to strongly attractive for those with seven sticky segments. In other words, weakly attractive multivalent polymers show a negative cooperativity for surface protection as the number of sticky segments increases. The negative cooperativity refers to the fact that, at a fixed polymer composition, addition of the binding sites leads to the weakening of surface attraction, in contrast to the cooperative behavior for those polymers with strongly binding sites. Because
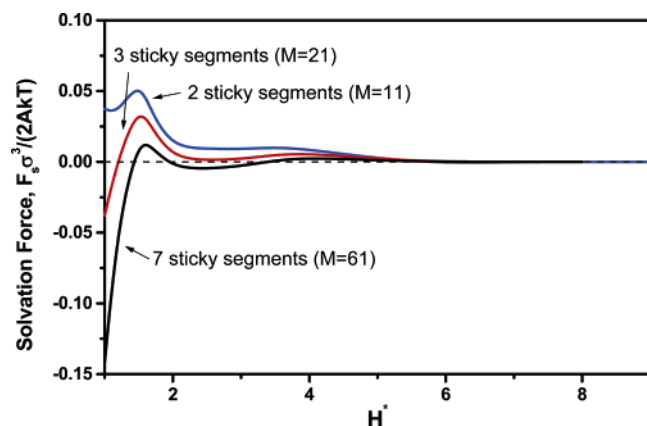
Figure 6. Solvation force due to multivalent polymers with weakly anchoring sites
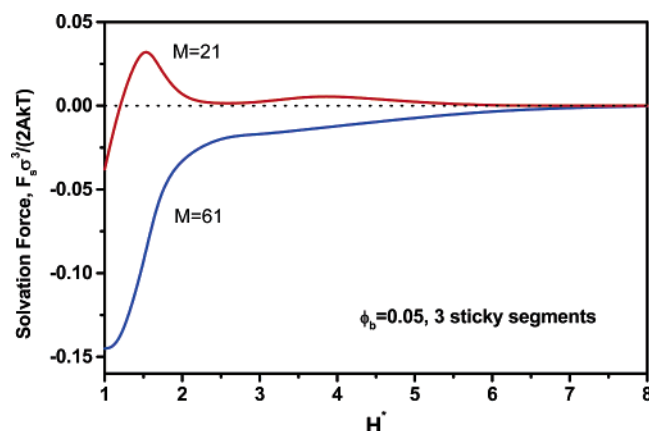

Figure 7. Effect of the length of the neutral block on the solvation force

a multivalent polymer includes surface tethering segments that favor adsorption and solvent-like blocks that favor depletion, the negative cooperativity arises when the tethering energy is insufficient to compensate the entropy loss due to immobilization of nonadsorption chains. As shown in Figures 2 and 4, the depletion attraction disappears as the anchoring energy for each sticky segment is sufficiently strong. Nevertheless, in both cases presented in Figures 4 and 6, M-type multivalent polymers with one loop (two sticky segments) are most efficient for surface stabilization.

Figure 7 shows the solvation forces due to two multivalent polymers with the same number of weakly anchoring segments but different lengths of neutral blocks. As expected, the range of attraction increases with the length of intermediate neutral segments. The solvation force is everywhere attractive for the polymers with 29 segments in each spacing neutral block ($M = 61$). For polymers with shorter neutral blocks ($M = 21$), however, the solvation force exhibits an oscillatory behavior, reflecting the subtle interplay of surface attraction, entropic depletion and bridging effects. Apparently, the attraction near contact is due to depletion of polymer chains. As discussed later, the two weakly attractive minima are related to the fluctuation of surface segments and bridging effects, respectively. Figure 7 suggests that multivalent polymers with weakly binding sites are probably not very useful for surface protection.

To provide further insights into the origin of solvation forces, we have also studied the microstructures of the multivalent polymers near each planar surface. Figure 8a shows the reduced density profiles of the sticky and neutral segments for M-type multivalent polymers as

discussed in Figure 7. When the separation is less than the range of surface attractions ($H^* = H/\sigma = 1$), the surface potential is uniform and thus the sticky and neutral segments exhibit identical density profiles. For larger separations ($H^* = 1.5$ and 4), however, the sticky segments are primarily located within the attractive well accompanied by a continuous distribution of the neutral segments. Figure 8b presents the density profiles of the end and middle segments of the neutral blocks (here the second and sixth segments). The polymer structure and its distribution within the slit are depicted in Figure 8, panels c and d. At a small separation ($H/\sigma = 1.5$), the density profiles of the end and middle segments of the neutral segments are nearly the same, suggesting a uniform distribution of polymeric segments due to the strong confinement. At large surface separations ($H/\sigma = 4$ and 8), however, the peaks in the density profiles of the end and middle neutral segments are separated, suggesting the formation of loop and bridge-like conformations.

The difference in the densities of the middle and end sticky segments at the center of two surfaces reflects the bridging of the multivalent polymer chains. At large surface separations, bridging is not possible, and the densities of the middle and end sticky segments at the center are the same. At small separations, on the other hand, essentially all polymer chains are in contact with both surfaces. In that case, we also expect no difference between middle and end segment densities. When bridging occurs, however, the density of the middle sticky segment is expected to be higher than that of the end sticky segments. Figure 9 shows the center-position densities of the end and middle sticky segments at various surface separations. When the separation is less than 3σ, essentially all sticky segments are located within the attractive wells of the confining surfaces so that their densities at the center are very small. Both the end and middle sticky segment densities increase with the surface separation but the density of the middle sticky segment always exceeds that of the end segment. At $H/\sigma = 6\sim7$, the difference between the two densities reaches a maximum. In comparison to Figure 7, it appears that bridging occurs at a separation when the overall solvation force is weakly attractive ($H^* \sim 6.5$). Conversely, the attraction due to the fluctuation of surface segments is most likely when the two layers of polymers are approximately at contact ($H^* \sim 2.5$). The attraction due to surface depletion occurs only when the surface separation is smaller than the polymer size ($H^* < 1.5$). In the case of surface depletion, the surface excess becomes negative (Figure 8b).

At fixed chain length, the solvation force is also sensitive to the number of sticky segments embedded in each polymer chain. In general, the more polymers that are adsorbed at each surface, the stronger the repulsion is. Figure 10 presents the solvation forces due to M-type multivalent polymers with 3, 7, and 11 surface binding segments at fixed total chain length $M = 61$. Introduction of more binding segments into the polymer chain enhances the surface adsorption and reduces the length of neutral blocks. Because of the weak surface attraction, the solvation force due to multivalent polymers with three binding sites is everywhere attractive, resembling that for nonadsorbing polymers. For polymers with 11 binding sites per chain, however, the depletion attraction diminishes. In this case, the weakly attractive minimum at large separation is probably due to the correlated fluctuations of the segmental density profiles. Figure 10 indicates that for multivalent polymers with fixed total chain length,
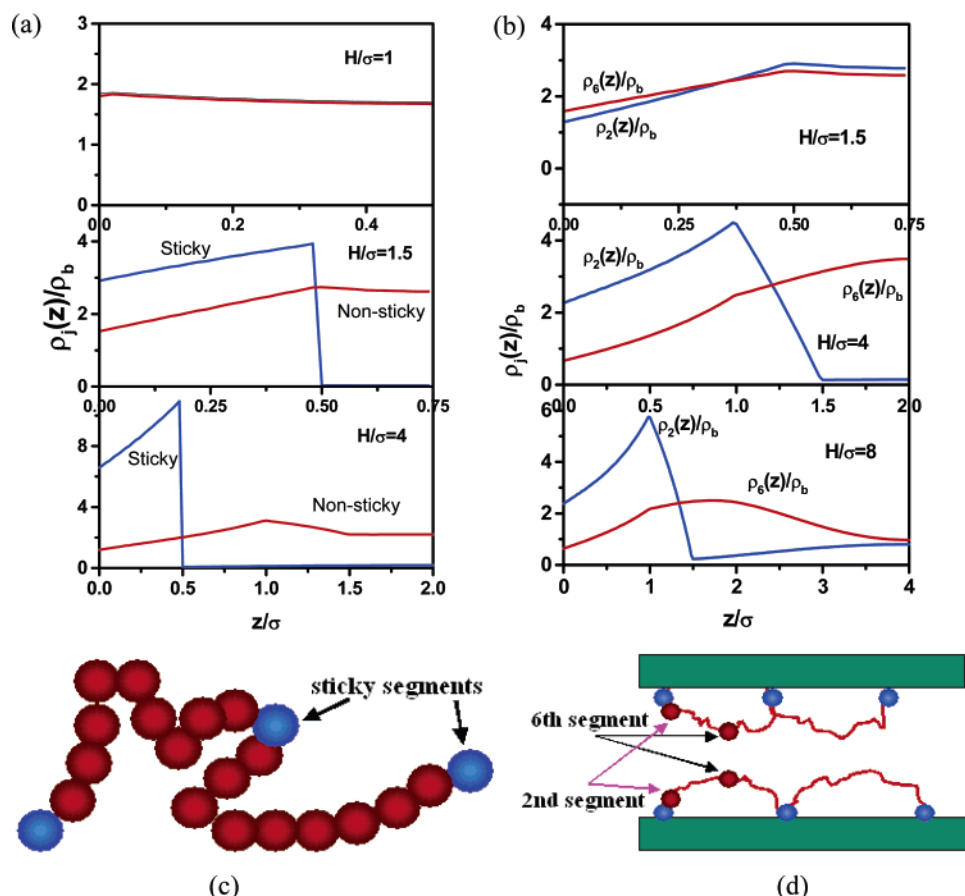
Figure 8. (a) Density profiles of sticky and neutral segments of the polymer with $M = 21$. (b) Density profiles of the end (2nd) and middle (6th) segments in the neutral block.
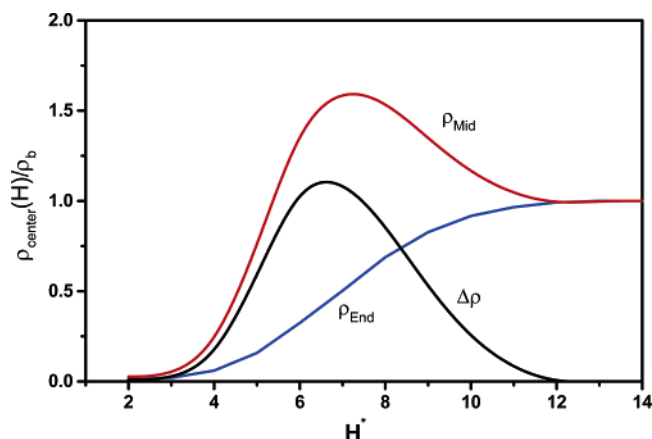

Figure 9. Middle-point densities of the end and middle sticky segments at different surface separations ($M = 21$).

Figure 10. Solvation forces due to multivalent polymers with different numbers of weakly anchoring sites.

addition of weakly anchoring segments improves the surface protection.

5. Conclusions

We have investigated the cooperativity of W- and M-type multivalent polymers in adsorption and colloidal stabilization based on a polymer density functional theory for coarse-grained polymer models. As demonstrated in recent experiments,[7] the W-type multivalent polymers exhibit a strong cooperativity; that is, polymers with multiple binding segments provide higher levels of surface protection than those with only one binding site. Conversely, for M-type multivalent polymers, polymers with two binding ends (e.g., telechelic copolymers) are more efficient than those with either one or multiple binding sites. Negative
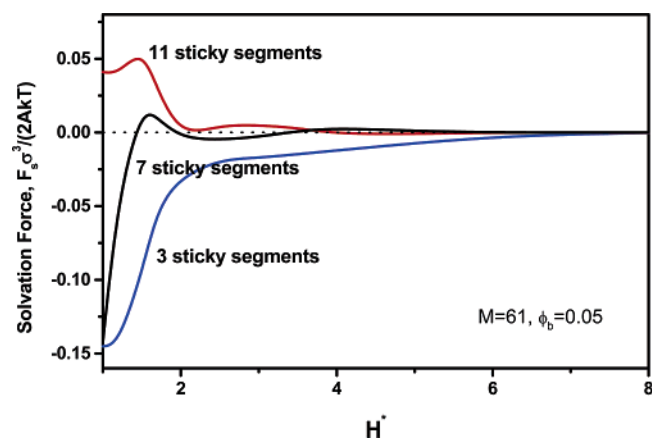
cooperativity is observed for the M-type architecture with weakly attractive anchoring segments. The increase of chain length at the fixed ratio of adsorbing and non-adsorbing segments leads to a stronger attraction due to the entropic depletion of long polymer chains. The theoretical results also indicate that at similar solution conditions and polymer composition, the solvation force due to M-type chains are much more repulsive than that due to W-type chains.