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Using End-Confined Chains To Model End-Absorbing, Triblock Copolymers: 1. Analytical Approach

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ABSTRACT: The bridging attraction, mediated by associative, triblock copolymers with insoluble end blocks and a soluble spacer block, is analyzed using scaling arguments and analytical methods. Adsorbing these associative polymers (APs) onto a single surface, the approach of another, bare, surface results in a strong bridging attraction. When both slit surfaces bear adsorbed APs, the bridging attraction is much weaker. The main contribution is an entropic gain since bridge formation decreases the monomer number density in the crowded region near the surface.

I. Introduction

An intriguing aspect of block copolymers is that their solution properties do not depend solely on the relative solubilities of their subunits. They also depend on the architecture, i.e., the length and position of the building blocks.[1−9] The number of design possibilities increases rapidly with the number of subunit types, as is amply illustrated by the great versatility of proteins where 20 amino acids are the building blocks. Common synthetic block copolymers usually have fewer building blocks, but the design possibilities are nonetheless numerous. A case of special interest is a “selective solvent”, i.e., when the building blocks have very different solubilities; copolymers are then surface active and may self-associate at some critical concentration. The simplest such block copolymer, the AB diblock (where A denotes an insoluble and B a soluble block) is a direct analogue of “ordinary” surfactants. Consequently, it exhibits a similar multitude of self-organized structures,[10] for example, spherical and rodlike micelles, lamellar phases, etc. For triblock copolymers, there is a choice whether to put the soluble or the insoluble blocks at the chain ends, denoted BAB and ABA, respectively.[11,12] The latter ABA copolymers exhibit a new degree of freedom (in addition to self-association) in that they may form physical bridges between aggregates. The consequent attractive force between aggregates, the “bridging attraction”, is the topic of this paper.

The ABA triblock copolymers belong to the larger class of associative polymers (APs).[13−16] (In general, APs may contain an arbitrary mixture of soluble and insoluble blocks.) APs are useful as rheological modifiers, as exemplified by water-borne paints, where the use of APs represents a major break through toward rheological properties close to those of traditional solvent-borne paints.[17−20] The dramatic changes of the physical properties caused by changes in the polymer architecture and/or the balance between the amounts of soluble and insoluble blocks provide for a great versatility of APs. The equally dramatic changes induced by additives, e.g., surfactants and colloid particles, are a mixed blessing and may cause major inconveniences in the practical use of APs.[18] The lack of a simple, comprehensible model hampers an understanding of their functional mechanism.[19,20] Nevertheless, recent developments in polymer theory[2,8,9,21−44] and simulation methods[3−6,45−55] are important steps in the right direction (the reference list is by no means exhaustive). If an appropriate model appears, a wealth of experimental data for several fairly well-defined ABA polymers, with and without the presence of surfactants, is available to test its qualitative predictions.[11,12,46,47,56−77]

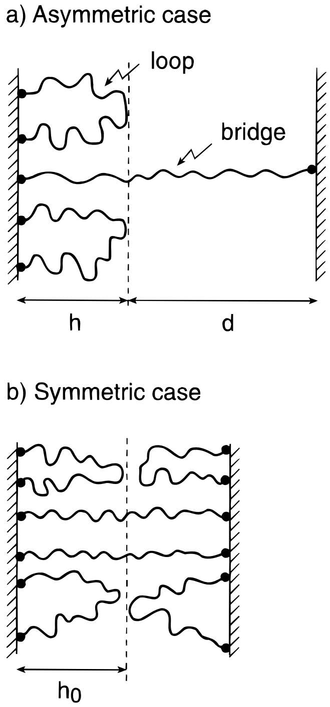

Figure 1. Schematic illustration of the case of asymmetric and symmetric grafting.

In the present series of two papers (see also the following paper in this issue), we focus on the entropic contributions to the bridging attraction between particles mediated by adsorbed ABA block copolymers in a selective solvent. After a few simplifying assumptions, we arrive at the simple mean-field model of end-confined chains in a slit that may be solved either by numerical methods or (with some additional assumptions) by analytical methods. We consider two arrangements, shown in Figure 1: asymmetric and symmetric surface coverage. The symmetric adsorption represents the equilibrium distribution of APs on the particles. The asymmetric case, interesting for adhesion applications,

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requires that one spacer end is chemically grafted onto the surface (a CBA block copolymer). However, the asymmetric case would also arise as an initial nonequilibrium state if new particles, for example, pigments, were added to a dispersion of AP-covered particles.

In this paper, we concentrate on an analytical approach due to Johner and Joanny (JJ)[22,23] and extend it to the above model systems. For the symmetric case, results previously obtained by Milner and Witten (MW)[21] and Semenov et al. (SJK)[24] are also discussed. Both of these approaches rest on the self-consistent mean-field theory for grafted chains independently developed by Milner et al. (MWC)[78] and Zhulina et al.[79] and on the proposed extension to loops later suggested by Milner and Witten.[21] In the second paper of the series (referred to below as paper 2 (the following paper in this issue)), numerical results lend further credibility to the analytical predictions.

The outline of this first paper is as follows: In section II, after a brief presentation of the model, the analytical approach is described. Some of the MWC[78] results (adapted to loops on a single surface) are restated as an introduction to the analytical solution for the cases of asymmetric and symmetric surface coverage. The symmetric case has previously been analyzed by MW[21] and SJK[24] and is only briefly presented. The results are then discussed in section III. The paper ends with some concluding remarks.

II. Theory

II.A. Description of the Model System. In order to model the interactions between particles mediated by adsorbed ABA block copolymers, a few simplifying assumptions are made:

(i) The particles have A-type surfaces and are large enough to be considered planar.

(ii) The length of the adsorbing A blocks may be neglected in comparison to the length of the B spacer blocks.

(iii) The selective solvent is good (B-type) for the B spacer block and the A blocks have a sufficiently strong affinity for the slit surfaces that the concentration of nonadsorbed ends may be neglected. Neglecting end-block self-association, the spacer ends are then confined to either of the surfaces. The B spacer blocks are thus forced either into loop conformations on the same particle or into bridge conformations between particles. Obviously, the equilibration process requires reversible adsorption of the spacer ends. Neglecting free ends only implies that the system properties are determined by the large majority of loop or bridge forming spacers.

(iv) Random mixing parallel to the planar slit surfaces reduces the many-chain problem to the statistics of a single chain in an average chemical potential field $U(z)$ acting on the segments. Since the model system is athermal, the energy of the model system is constant and independent of the spacer conformations. The free energy changes that occur (in the model) when two particles with adsorbed ABA copolymers approach each other are therefore entirely of entropic origin.

The first three assumptions effectively reduce the model system to a collection of end-confined B spacer blocks immersed in a B-type solvent in a planar slit with A-type surfaces. Each spacer block consists of N segments of B monomer and is approximated as a "string-of-(N)-pearls", where each "pearl" of unit volume is separated by a string (bond) of unit length. The fourth assumption simplifies the statistical mechanical treatment. The main drawback with this simplification is that the mutual exclusion of segment pearls must be approximated in some way. Therefore, the description of a conformation is reduced to the mere sequence of layers with constant z, where the consecutive segments are located (z is the coordinate perpendicular to the planar slit walls with $z = 0$ at the wall).

Since the above model is athermal, the mean-field $U(z)$ only depends on the system constraints and the mutual excluded volumes of the monomers. (Note that $U(z)$ should not be confused with energy per se.) Unfortunately, an athermal solvent is too good. The strong coupling between $U(z)$ and the local monomer density $\Phi(z)$ prevents a direct analytical solution. In a marginal solvent, on the other hand, this coupling is turned down toward the limiting case of a Θ solvent, where the first order coupling vanishes. In a marginal solvent, a mean-field $U(z)$ proportional to the $\Phi(z)$ is therefore an acceptable approximation. In this case, it is straightforward to obtain complete analytical solutions (i.e., scaling exponents *and* constant prefactors) within the MWC[78] assumptions. In a good solvent or when self-interaction is important (for small $\Phi(z)$), it is more appropriate to use a blob picture of the chains. In this approach, it is the scaling exponents that are most easily obtained. Therefore, the strategy below is first to solve the case of a marginal solvent and then to generalize to the good (athermal) solvent case.

II.B. Loops on a Single Surface. Marginal Solvent. Consider a slit surface with spacer loops, that is, when the other slit surface is sufficiently remote so that no bridges can form. A key step in the following analytical treatment is the artificial introduction of "free" ends obtained by cutting the loops into two grafted half-chains of length $N/2$.[21] The main advantage of this approximation is that the analytical theory for grafted chains, pioneered by MWC[78] and others, may be used. (The presentation in MWC,[78] adapted to loop half-chains, is essentially followed in this section.) The half-chain approximation assumes that the end points of the two loop half-chains are independent of each other even though they supposedly represent a loop. This approximation is critically examined using the numerical approach in paper 2 and is found to be fairly good. A second ingredient is the assumption that the grafted half-chains are crowded enough to stretch significantly. If, in addition, the half-chains are long, there exists an analogy[78,80] between a chain conformation and the classical path (*from* the chain-end position *to* the grafting surface) of a "fictitious" particle of unit mass moving in a mean-field potential $U(z)$. In this analogy, the chain length and local tension of the grafted chains play the roles of "time" and "velocity" in classical mechanics, respectively.

For the analogy to be valid, some constraints are imposed on $U(z)$. First, since the half-chains have the same length ($N/2$), the time integral along a particle path must be the same for all paths regardless of starting position. Second, the artificially introduced "free" chain ends cannot support any tension, so all particles must start at zero velocity. These two requirements force $U(z)$ to be of the same functional form as a harmonic spring potential (where all motions indeed have the same period (T_p) regardless of the starting position of a particle originally at rest). Consequently, $U(z)$ is parabolic with a minimum at $z = 0$ and has the form $U(z) = -(A - Bz^2)$, where B is related to the spring constant by $k_s = 2B$. Since the period of harmonic motion is given by $2\pi/T_p = (k_s/m)^{1/2}$ and our fictitious particle of unit mass only performs a quarter cycle (moving along a half-chain of length $N/2$ from the chain-end position to the grafting surface) so that $T_p = 4(N/2)$, then $B = \pi^2/(2N^2)$. For chains immersed in a marginal solvent, MWC[78] and Zhulina et al.[79] have shown that

$$U(z) = -(A - Bz^2) = -w\Phi(z) \tag{1}$$

where $w(T)$ is a temperature-dependent constant related to the solvent−monomer interaction strength. Obviously, $\Phi(z)$ also has a parabolic shape for a grafted brush in a marginal solvent.

Equation 1 forms a self-consistency loop, and the parameter A may be determined by the conservation of monomers in the parabolic brush, i.e., in the region where eq 1 holds. When no bridges are formed, all of the segments are located in the parabolic brush and the monomer density vanishes at a distance that is defined as the half-chain brush height h_0. Consequently, the constant A for loops on a single surface may be written as $A_0 = Bh_0^2$. Equating the integral of the monomer density in the parabolic region with the total number of segments per unit area ($N\sigma$), h_0 becomes

$$h_0 = \left(\frac{3N\sigma w}{2B}\right)^{1/3} = \left(\frac{3\sigma w}{\pi^2}\right)^{1/3} N \tag{2}$$

where σ is the number of spacers per unit area of the grafting surface.

The chemical potential (action) of a half-chain with a given conformation ($z(n)$, $n \in [0, N/2]$) corresponds, in the analogy, to the constant total energy given by the sum of the kinetic and potential energies along the classical path. Since the path for our classical fictitious particle satisfies the equation of motion (see MWC[78]), we have $z(n) = z(N/2)\sin(n\pi/N)$. The path is thus completely specified by the location of the free chain end. Furthermore, the particle moves continuously toward the grafting surface so that a half-chain never contributes to the monomer density beyond the location of its free end. At equilibrium, all chains have the same chemical potential irrespective of their conformation, so it is sufficient to evaluate the total energy for a single path. A particularly simple choice of path is obtained when the fictitious particle starts at the grafting surface ($z = 0$). Such a particle obviously remains at rest ($z(n) = (\mathrm{d}z(n)/\mathrm{d}n = 0, \forall n)$, and the chemical potential can be evaluated directly. The chemical potential for the loops, twice that for the half-chains, then becomes

$$\beta\mu_0 = NA_0 = NBh_0^{\,2} = {}^1/_2(3w\pi\sigma)^{2/3}N \tag{3}$$

where $\beta = 1/(k_BT)$, k_B is Boltzmann constant, and T is the absolute temperature. Since the free energy cost (G) of building up a loop brush is given by $\mathrm{d}G = \mu(\sigma)\,\mathrm{d}\sigma$, the free energy per spacer loop is

$$\beta F_0 = \frac{\beta G}{\sigma} = \frac{3}{10}(3w\pi\sigma)^{2/3}N \tag{4}$$

Good Solvent. In a good solvent for the half-chains, that is, for the loops on a single surface, the chains extend further into the solution. According to MWC,[78] the brush height and the free energy per spacer then scales as

$$h_{0g} = C_1 N\sigma^{(1-\nu)/((d-1)\nu)} \approx C_1 N\sigma^{0.350}$$
$$F_{0g} = C_2 N\sigma^{1/((d-1)\nu)} \approx C_2 N\sigma^{0.850} \tag{5}$$

where C_1 and C_2 are constants and where the Flory exponent $\nu = 0.588$ and the dimension $d = 3$ are chosen for the last step. The constants C_1 and C_2 are not strictly universal and depend on microscopic parameters such as persistence length, etc. Comparing eqs 2, 4, and 5, the quality of the solvent primarily determines the scaling behavior with respect to σ.

II.C. Loops and Bridges in a Slit. Asymmetric Case. For the asymmetric case (where all spacers are confined to start with one end on the same slit surface), a previous treatment by JJ[22,23] is adapted to the case of loop half-chains of length $N/2$ and bridges of length N. The treatment assumes a marginal solvent, but the results valid for a good solvent are conjectured at the end of the section. When the other, bare, surface is close enough, bridges between the surfaces are formed and loops and bridges will coexist. By analogy, this corresponds to the coexistence of two types of particles, loop and bridge particles, experiencing different path constraints. Nevertheless, as a consequence of the constant length of the loops and the tension-free half-chain ends, the "equal time" requirements still apply for the loop particles. The potential $U(z)$ therefore remains parabolic in the region where the free ends are located. In this region, eq 1 is still valid even though $\Phi(z)$ includes contributions from the bridges.

Both bridge ends are obviously fixed onto the surfaces, so beyond the parabolic region there exists a so-called "dead" zone where no free chain ends are present.[22,23] Now suppose that bridge particles start from the chain end at the bare surface with a certain density (σ_b), i.e., where a specified fraction ($\eta = \sigma_b/\sigma$) of the spacers forms bridges. Since the surfaces are held at a constant separation D, bridge ends are subjected to a tension τ. By the above analogy with classical mechanics, the "bridge" particles starting from the bare surface ($z = D$) will possess an initial velocity toward the grafting surface ($\tau \leq 0$). Both types of "particles" move continuously from larger to lower z, so the contributions to the monomer density at z only come from chains with ends beyond z (see section II.B). $\Phi(z)$ may in fact be expressed in terms of chain-end densities $\epsilon(z')$, $z' \geq z$, as[78]

$$\Phi(z) = \int_z^D \mathrm{d}z'\,\epsilon(z')\left|\frac{\mathrm{d}z}{\mathrm{d}n}(z';z)\right|^{-1} \tag{6}$$

where $\mathrm{d}z/\mathrm{d}n(z';z)$ is the local velocity at z, given that the particle started at z'. Given the initial velocities at z' for the loop and bridge particles, 0 and τ, respectively, the local velocity $\mathrm{d}z/\mathrm{d}n(z';z)$ may be solved for by equating the total energy at z and z'. Since the chain-end density for loop half-chains vanishes beyond the loop brush height (h), only bridges will contribute to the monomer density in the dead zone ($h \leq z \leq D$). Furthermore, since the chain-end density for the bridges is given by a δ-function as $\epsilon(\tau) = \delta(D - z)\sigma_b$, the monomer density in the dead zone is a constant given by

$$\Phi(z) = \Phi_{\mathrm{d}} = \frac{\sigma_{\mathrm{b}}}{|\tau|} = \frac{P\eta\sigma}{d}, \quad h \le z \le D \tag{7}$$

where h is the width of the parabolic zone (loop brush height), $d = D - h$ is the width of the dead zone, and P denotes the number of monomers per bridge located in the dead zone. The latter relationship in eq 7 is obtained from the conservation of bridge monomers in the dead zone giving the tension as $|\tau| = d/P$. Using eq 6 and conservation of total energy for the bridge particles, the contribution from bridges to the monomer density in the parabolic region is given by

$$\Phi_{\mathrm{b}}(z) = \sigma_{\mathrm{b}}[2B(h^2 - z^2) + (d/P)^2]^{-1/2} \tag{8}$$

where $B = \pi^2/(2N^2)$ for half-chains (see the previous section). From eq 8 and onward, my results differ from JJ.[22,23] In the present model, a bridge is twice the length of a loop half-chain. In the JJ treatment they have equal lengths.

Using eq 8 and conservation of bridge monomers in the parabolic region now gives the identity

$$\frac{d}{h} = -\left(\frac{P\pi}{N}\right)\cot\left(\frac{P\pi}{N}\right) = -y\cot(y), \quad \frac{\pi}{2} \le y \le \pi \tag{9}$$

where the latter equality defines the convenient substitution,[22,23] $y = P\pi/N$. The lower limit of validity is obtained if half of the bridge is located inside the parabolic region, i.e., $\tau = 0$. Obviously, P can never exceed N, which gives the upper limit. Equation 9 gives d, and consequently the tension τ, as a function of P only. The equilibrium P, or rather y, may now be obtained by equating the chemical potential for the loops and the bridges.

Combining eqs 1 and 7 gives $A = Bh^2 + w\Phi_{\mathrm{d}}$, and, in analogy with eq 3, the chemical potential for the loops is obtained directly as

$$\beta\mu_{\mathrm{l}} = NA = N(Bh^2 + w\Phi_{\mathrm{d}}) \tag{10}$$

Since all bridge particles follow the same path (they all start from the same position), no simple path may be chosen. The chemical potential for bridges is thus given by the total energy of the bridge path. The contribution to the chemical potential from the P bridge monomers in the dead zone is given by the sum of the constant kinetic and potential energy given by $\tau^2/2$ and $w\Phi_{\mathrm{d}}$, respectively. In the parabolic region, the bridge path is given by the equation of motion as $z(n) = (h/\sin(y))\sin(n\pi/N)$ for $(0 \le n \le N - P)$. The contribution from monomer n to the chemical potential in the parabolic zone is given by the kinetic energy $^1/_2[\mathrm{d}z(n)/\mathrm{d}n]^2$ and the potential energy $U(z(n))$. Summing the contributions (by integrating over dn), the chemical potential for the bridges becomes

$$\beta\mu_{\mathrm{b}} = \beta\mu_{\mathrm{l}} + \beta\Delta = \beta\mu_{\mathrm{l}} + \frac{h^2\pi}{4N\sin^2(y)}(2y\cos(2y) - \sin(2y)) \tag{11}$$

where eqs 7, 9, and 10 together with $y = P\pi/N$ and trigonometric identities were used.

At equilibrium the chemical potentials of bridges and loops are equal, i.e., $\beta\Delta = 0$, and numerical solution yields $y \approx 2.2467$, a surprising and interesting result! Provided that bridges are formed, they always distribute a constant fraction ($P/N \approx 0.71515$) of their monomers to the dead zone regardless of the actual surface separation (D) or the extent of crowding on the grafting surface (σ). Thus only 28.5% of the bridge monomers remain in the parabolic region. In addition, when bridges exist, d/h (eq 9) is a constant ratio so that d and h are constant fractions of D given by

$$d = \frac{y}{y + \tan(y)}D \approx 0.64307D \tag{12}$$

$$h = \frac{1}{1 - y\cot(y)}D \approx 0.35693D \tag{13}$$

When the surface separation is sufficiently large, so that no bridges are formed, then $d = 0$ and $h = h_0$. Thus, no bridges can form beyond a surface separation

$$D_0 = [1 - y\cos(y)]h_0 \approx 2.80167h_0 = 2.80167\left(\frac{3w\sigma}{\pi^2}\right)^{1/3}N \tag{14}$$

Here the brush height for the unperturbed loops (h_0) obviously plays the role of a universal (natural) length scale. As expected, D_0 increases for longer and more crowded spacers. At smaller separations, the equilibrium fraction of spacers forming bridges can be evaluated using the conservation of the total amount of monomers in the parabolic region as

$$\eta_{\mathrm{asym}} = \frac{\pi}{y - \tan(y)} - \frac{D^3}{h_0^{\,3}}[(1 - y\cot(y))^3(y - \tan(y))]^{-1} \approx 0.89921 - 0.040890\frac{D^3}{h_0^{\,3}} \tag{15}$$

Note that choosing the separation in units of the natural length scale (D/h_0) results in a universal function valid for all N and σ. Whereas the upper limit for the validity of eq 15 is D_0, the lower limit is attained when the assumptions leading to a parabolic region break down.

Combining eqs 7, 12, and 15, the volume fraction in the dead zone may now be determined

$$\Phi_{\mathrm{d}} = \frac{N\sigma}{h_0}\left(\frac{h_0}{D} - \frac{D^2}{h_0^{\,2}}[1 - y\cot(y)]^{-3}\right) \approx \frac{N\sigma}{h_0}\left(\frac{h_0}{D} - 0.045473\frac{D^2}{h_0^{\,2}}\right) \tag{16}$$

again given as a function of natural length D/h_0.

In order to evaluate the free energy per spacer chain of length N at some given separation $D \le D_0$, i.e., when bridges exist, one must realize that bridges are formed only if a minimum graft density given by eq 14 is attained

$$\sigma_0 = \frac{\pi^2}{3w}\left(\frac{D}{N[1 - y\cot(y)]}\right)^3 \approx 0.14960\frac{D^3}{wN^3} \tag{17}$$

The integral over σ therefore must be performed in two steps. For $\sigma' < \sigma_0$ the chemical potential for the spacer chains is given by eq 3 and for $\sigma_0 \le \sigma' \le \sigma$ by eq 10. The free energy per spacer chain becomes

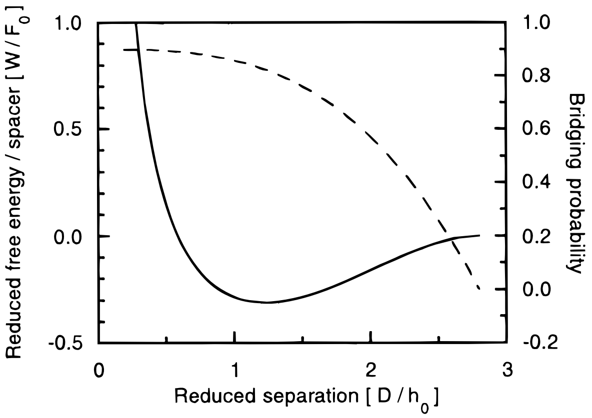

Figure 2. Theoretically predicted universal curves for the asymmetric case corresponding to the reduced free energy per spacer W_{asym}/F_0 (eq 19, full line) and the bridging probability (eq 15, dashed line) as a function of the reduced separation D/h_0.

$$F_{\mathrm{asym}} = F_0\left(\frac{5h_0}{9D} + \left(\frac{5(y\tan^2(y) - \tan^3(y)/3)}{3(y - \tan(y))^3}\right)\left(\frac{D}{h_0}\right)^2 - \left(\frac{\tan^5(y)[2y/3 - \tan(y)/9]}{(y - \tan(y))^6}\right)\left(\frac{D}{h_0}\right)^5\right) \approx F_0\left(\frac{5h_0}{9D} + 0.16181\left(\frac{D}{h_0}\right)^2 - 0.0027134\left(\frac{D}{h_0}\right)^5\right) \quad (18)$$

where the free energy per chain in the unperturbed loop brush emerges as the natural unit of free energy. The free energy of interaction between the two slit surfaces *per spacer chain* becomes

$$W_{\mathrm{asym}} = F_{\mathrm{asym}} - F_0 \approx F_0\left[\frac{5h_0}{9D} + 0.16181\left(\frac{D}{h_0}\right)^2 - 0.0027134\left(\frac{D}{h_0}\right)^5 - 1\right] \quad (19)$$

(Note that $W_{\mathrm{asym}}\sigma$ is the free energy of interaction per unit surface.) Equation 19 shows that using the natural units for free energy and length gives a universal curve independent of N and σ. In Figure 2, the universal free energy of interaction (eq 19) and the corresponding universal bridging probability (eq 15) are plotted as a function of surface separation in natural length units. The universal minimum in eq 19 is at (1.23, −0.311) in natural units.

The universal relations found for the system properties in eqs 12−19 suggest a simple extension to the case of a good (athermal) solvent. To a first approximation, the universal functions may be assumed to be unaffected by the solvent quality. It then suffices to substitute the natural units h_0 and F_0 by h_{0g} and F_{0g} (eq 5) to get the results valid in a good solvent.

Symmetric Case. The symmetric case corresponds to an equilibrium distribution of nongrafted APs. Since symmetry allows insertion of an imaginary wall at the midpoint between the surfaces, each resulting system half can be treated as above. However, the bridges are cut in half by the imaginary wall and thus have the same length ($N/2$) as the loop half-chains. Equating the chemical potential for loops and bridges in this imaginary *asymmetric* system, as above, does not lead to an attractive force. Bridges begin to form only when $D \leq 2h_0$. In a marginal solvent, the free energy of interaction becomes

$$W_{\mathrm{sym}}^{\mathrm{classical}} = F_{\mathrm{sym}}^{\mathrm{classical}} - F_0 = F_0\left[\frac{10}{9}\left(\frac{h_0}{D}\right) + \frac{5}{36}\left(\frac{D}{h_0}\right)^2 - \frac{1}{288}\left(\frac{D}{h_0}\right)^5 - 1\right] \quad (20)$$

in the same natural units as for loop half-chains above. Equation 20 may also be obtained from the JJ results with an end-attachment energy of zero or by adapting the expression for the compressed brush derived by MWC[78] and MW[21] to the case of half-chains. In the classical limit, when the thermal fluctuations around the classical paths have been neglected, the force between surfaces with symmetrically adsorbed APs is thus purely repulsive. However, attractive forces do arise if the treatment is extended to include fluctuations,[21,24] but these relatively weak forces only act in the vicinity of classical contact.

III. Results and Discussion

III.A. Bridging-Attraction. At slit separations where bridges may be formed, the added degree of freedom leads to a “bridging attraction” between the slit surfaces.[81,82] The attraction is particularly strong when one of the surfaces is bare, i.e., bears no adsorbed spacers. In this asymmetric case, bridges start to form at a surface separation 2.8 times the loop half-chain brush height (eq 17), even though the bridging spacers become more stretched than in a loop conformation. On the other hand, stretching the bridges effectively removes bridge monomers from the crowded loop region. The loop stretching can be relaxed, and the overall free energy is lowered. According to the analytical treatment above, only 28.5% of the bridge monomers reside in the loop (parabolic) region and the rest (71.5%) reside in the dead zone. Remarkably, these fractions are completely independent of the degree of crowding (N and σ) and of the surface separation $D < D_0$.

Another remarkable prediction is that the loop brush height h (in the presence of bridging spacers) is independent of N and σ and varies linearly as $h = 0.36D$ (eq 12) with the surface separation when $D < D_0$. Thus, the width of the dead zone also varies linearly $d = 0.64D$ (eq 13). When the approaching surface also bears adsorbed spacers, the tendency to form bridges and the bridging attraction decrease.

III.B. Short Loops Preferred. The scaling of the loop free energy in eq 5 also allows quite a general discussion of polymer adsorption. Consider, for example, the issue of whether a multiblock copolymer prefers to form long or short loops on a surface. Equation 5 implies that short loops are preferred. Converting a loop of length N into two loops of length $N/2$ decreases the free energy by 10%, that is, from $C_2N\sigma^{0.850}$ to $2^{-0.15}C_2N\sigma^{0.850}$. The preference for short loops has also been conjectured by Cates and Witten[2] and is supported by the theoretical results of Jacobson and Stockmayer,[83] ten Brinke and Hadziioannou,[34] and Balsara et al.,[36] as well as by the simulation results of Baljon,[4] Wang et al.,[45] and Nguyen-Misra and Mattice.[51]

Consequently, consecutive insoluble blocks in a multiblock copolymer tend to associate into flowerlike, intramolecular, micellar aggregates, since such an arrangement gives the smallest loops.[28−30] Another example is provided by a polyelectrolyte chain interacting with an oppositely charged micelle.[84] The driving force for ever smaller loops leads to a tendency for the polyelectrolyte chain to wrap around the micelle as tightly as its flexibility and the separation between the charges allow. In a qualitative sense, a homopolymer would also prefer a collapsed adsorption conformation based on the same arguments, leaving only the chain ends protruding outward from the surface. When the surface becomes increasingly crowded with adsorbed polymer and a collapsed state no longer is possible, the free energy of adsorption decreases (provided that no cooperative effect exists). At this point, the maximum adsorbed amount is reached. The latter explains a curious effect in triblock (and diblock) adsorption first found by Evers et al.:[7,8] For a given length of the spacer block there exists an optimum length of the end blocks, giving the greatest adsorbed amount.

IV. Conclusions

A model of an associative polymer (AP) as an end-absorbed spacer has been introduced and analyzed. (The conclusions are further supported in a subsequent paper 2 using a numerical approach.)

In particular, I present an analytical treatment of AP spacers immersed in a marginal solvent in an asymmetric slit. One spacer end is then assumed to be grafted onto one of the slit surfaces, and the other end is restricted either to form loops on the same surface or bridges to the other, bare, surface. The asymmetric slit is obviously not the equilibrium situation for physically adsorbed AP spacers. However, it may be of considerable practical interest as an initial quasi-equilibrium state. If the A-block adsorption strength is greater than or equal to 5 k_BT, as indicated by the simulations of Wittmer et al.,[85] the dynamics of desorption is sufficiently slow to allow for relaxation of the brush. If the dynamics of desorption is slow, equilibration by migration of APs to the bare surface will be orders of magnitude slower. It is therefore likely that this quasi-equilibrium state is fairly long-lived.

The bridging-attraction is shown to be particularly strong in the case of asymmetric slit coverage. The formation of bridges pulls monomers out of the crowded parabolic region into the dead zone and provides the entropic driving force for the bridging attraction. Unexpectedly though, the bridges leave a constant fraction (28.5%) of its monomers in the parabolic region irrespective of the degree of crowding (N and σ) or of the slit separation ($D < D_0$). Another remarkable prediction is that the width of the parabolic region and dead zone only depends on the separation D; i.e., $h = 0.36D$ and $d = 0.64D$, when $D < D_0$. Choosing the natural units of length and free energy to be the loop brush height and the free energy per spacer of the undisturbed loops (eqs 2 and 4 for a marginal solvent) results in universal functions for the system properties. To a first approximation, the generalization to a good (athermal) solvent is accomplished by changing the scaling of the natural units (to that in eq 5).

Even though the asymmetric case is an interesting special case, the symmetrical case is the equilibrium situation for physically adsorbed APs. In the symmetric slit, the bridging attraction is much weaker than in the asymmetric slit. The symmetric case may be described as an asymmetric case where the length of the bridges is $N/2$, rather than N. In the classical limit, this subtle difference leads to a purely repulsive interaction in the symmetric case. However, a weak bridging attraction emerges, in the vicinity of brush contact, when k_BT fluctuations are considered.

The scaling of the free energy of the undisturbed loops predicts that adsorbed polymers with “sticky” sites prefer to make loops as short as possible. This argument may be extended to rationalize the existence of an optimum end-block length, giving the maximum adsorbed amount of triblocks and diblocks.

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