Bridging Attraction by Telechelic Polymers

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ABSTRACT: Telechelic polymer chains, having a strongly adsorbing group on each end, can induce attractions between surfaces to which the end groups adsorb by forming "bridges" spanning the two surfaces. However, such chains may also adsorb on a single surface, forming a "brush" of stretched loops; this leads to repulsive interactions between surfaces, as the brushes resist compression and overlap. We show that bridging leads to a weak attractive minimum in the interaction energy between parallel surfaces of strength $1.0 \times T(R/h)^2$ per chain (where R is the free radius of a chain and h is the height of an isolated brush) for two brushes just in contact. We explore the consequences of this attraction for colloid stability, experiments using the surface forces apparatus, and telechelic chains in melt conditions including multiblock lamellar phases.

Introduction

Amphilphilic polymers often adsorb selectively on surfaces, with, e.g., the polar moieties strongly adsorbed while the nonpolar parts are effectively repelled from the surface. In general, adsorbed polymers induce an interaction between two such surfaces. This interaction is attractive with homopolymers in equilibrium.[1] It is repulsive with simple amphiphilic chains with one adsorbing site apiece.[2-5] But when the chains have two or more adsorbing sites, the sign of the interaction is less clear. Here, the chains may bridge between the two surfaces, with an adsorbing group on each surface. Intuitively, this bridging produces an attraction between the surfaces, which competes with the repulsive force characteristic of chains with a single adsorbing group. The outcome of this competition is of broad significance, since it bears on the phase stability of colloids in any liquid containing amphiphilic polymers.

In this paper we explore this competition in a tractable and experimentally relevant limit. We consider "telechelic" polymers, which adsorb strongly by small groups at either end. The interaction induced by such polymers has been studied recently by Dai and Toprakcioglu[6] using the surface forces apparatus. When the adsorption interaction is strong, the chains attach to the surface so densely that the nonadsorbing parts crowd together and distort one another. The grafting density rises until the adsorption energy is balanced by the crowding energy of the distorted chains.

In principle this energy may reach many times the thermal energy kT per chain and thus produce an arbitrarily strong distortion of the chains. In current experiments this energy appears to attain several kT.[3,7] The distinctive scaling behavior of this "brush" state was worked out by Alexander[8] and de Gennes.[9] The statistical mechanics of the crowded chains takes a simple and distinctive form which has been much exploited recently.[10-14] The monomer density profile has a universal shape; the density becomes exponentially small beyond a particular height h.

The interaction induced by telechelic chains takes on a simple form in this limit. We find that the interaction has an attractive minimum near the brush-contact separation $2h$. The strength of this attraction is of order $kT(R/h)^2$ per adsorbed chain, where $R \sim N^{1/2}$ is the unperturbed chain dimension and N is the chain contour length. This is small for strongly-stretched chains, for which $h \gg R$. Recently, Ligoure et al. have studied this attraction by another approach.[15]

This paper is organized as follows. In section 1 we define the system explicitly and discuss the force between surfaces in general terms. We show that, at distances where the bridging attraction is important, the dominant contributions to the force may be expressed in a simple way in terms of a reference system of single-ended chains. In section 2 we use these expressions involving the reference system to obtain an explicit formula for the interaction energy for surface separations well beyond the attractive minimum.

In section 3, we employ numerical self-consistent field calculations for telechelic chains (with each end obliged to be on one or the other surface) to compute the interaction energy between surfaces in the vicinity of the attractive minimum; in section 4 we extend the scaling laws for the fraction of bridges and the depth of the attractive minimum to the cases of good solvents and telechelic chains in melt conditions. Finally, in section 5 we examine the implications of the present work for colloid stabilization and for experiments using the surface forces apparatus.

1. Types of Interaction

Our system consists of flexible linear polymers in a good solvent. Each chain has an adsorbing group on both ends. The solution also contains two flat, parallel surfaces of area A at separation d—one on the left and one on the right. The adsorbing groups have a strong attraction for the surfaces, so that essentially all ends are adsorbed to one surface or the other. (It is demonstrated in Appendix A that, in equilibrium, the fraction of singly-attached chains is small for strongly-adsorbing groups and/or low solution concentrations of the telechelic chains.)

It proves convenient ot discuss the telechelics in terms of a reference system of single-ended chains. We obtain these reference chains by cutting the telechelics into equal halves. We suppose that the reference chains have contour length N and an unperturbed root-mean-square end-to-end distance $R \sim N^{1/2}$, so that without excluded-volume effects the energy to stretch a reference chain to a distance h is ${}^3/_2 kT(h/R)^2$. (The telechelic chains have length $N_t = 2N$; we will work in terms of R and N throughout this paper.)

The repulsive part of the interaction between surfaces induced by telechelics is well described by the purely repulsive interactions between two reference brushes composed of the singly-adsorbing half-chains. The attractive part of the interaction results from the increased entropy when telechelic chains are able to form bridges between surfaces in addition to the loops formed on isolated surfaces. We examine the repulsive and attractive interactions in turn.

When these reference chains are introduced into our solution in place of the telechelic chains, their functionalized ends adsorb strongly to the two surfaces. The result is two opposing grafted polymer layers or "brushes" of some height $h \gg R$. The height h depends on the molecular weight of the polymers, the strength of adsorption, and the solvent quality; in the strong-stretching limit,[11] h scales as $h \sim N(w\sigma)^{1/3}$, where w is an excluded-volume parameter and σ is the coverage, defined here as the number of half-chains per unit area on a single surface. (The number of telechelic chains per unit area between the two surfaces is also σ.) The monomer density profile changes qualitatively at the height h: for heights z less than h, the density is roughly parabolic, extrapolating to zero at height h.[11] For heights beyond h, the density falls exponentially with height, with a penetration length ξ much less than h, as detailed below.

The quantitative form of this density depends slightly on the quality of the solvent. If the solvent quality is very good or the distance x between grafted chains is very large, then there can be substantial swelling of chain segments of size x. Then the interaction between the chains must be described by semidilute scaling laws[16] and Pincus-blob elasticity.[17] These scaling effects influence the concentration profile $\phi(z)$ only slightly, and they are relatively complicated to treat.[11] Accordingly, we consider the simpler regime of less good solvents, in which chain swelling may be neglected on the scale x. Semidilute chains in such "marginal" solvents are Gaussian at all length scales. However, they are dilute enough so that the work $\mu(z)$ done against osmotic pressure to add a monomer at height z is proportional to the local concentration $\phi(z)$.[18]

Under marginal solvent conditions, the chemical potential profile approaches the parabolic form $\mu(z)N = 3\pi^2/(8R^2)(h^2 - z^2)$ for a chain of N monomers.[11] Here and in what follows all energies are in units of the thermal energy kT. Evidently, the interaction energy of a chain in the brush is of order $\mu(0)N$; this in turn is of the order of the elastic energy of a Gaussian chain stretched to height h. Each is much larger than kT.

When the two surfaces are brought to distances $d < 2h$, the brushes are further concentrated, and additional work must be done against osmotic pressure. The resulting energy of compression is of the order μN per chain and is hence much larger than kT whenever the compression factor $2h/d$ is significantly greater than unity. This implies a substantial repulsive force. Well beyond the contact separation $d > 2h$, there is still a slight repulsion, owing to the interaction of the exponential tails of the concentration profile. Evidently this interaction is exponentially small in $d - 2h$; here the interaction causes indefinitely little perturbation of one brush on the other. Thus one may compute the interaction energy by accounting for the work required to introduce the monomers from the right-hand brush, at concentration $\phi_R(z)$, into the tail of the left-hand brush. The interaction energy per unit area may thus be written

$$V(d) = \int \mathrm{d}z\, \mu_L(z)\, \phi_R(z) \tag{1}$$

where $\mu_L = w\phi_L$ is the chemical potential owing to the monomers of the (unperturbed) left-hand brush. Evidently the interaction between the reference brushes is repulsive at all distances.

It remains to account for effects in the telechelic brushes not present in the reference brushes. The configuration of a given telechelic chain may be regarded as the configurations of a pair of half-chains with their free ends both located at the midpoint (location of the Nth monomer) of the telechelic chain. If the telechelic chain forms a loop, each half-chain is attached to the same surface; if it forms a bridge, the two half-chains are attached to opposite surfaces.

If telechelic chains are free to form bridges between the surfaces, and a fraction f actually do so in equilibrium, the ratio of Boltzmann weights for forming bridges versus loops must be $B_b/B_l = f/(1-f)$. Then the single-chain partition sum Z_s over loop and bridge configurations (with B_l set to unity) is just $Z_s = 1/(1-f)$, and the bridging attraction per chain is $F = -k_BT \log Z_s \approx k_BTf$, where we have assumed $f \ll 1$. So we expect an attractive free energy of the order of the number of bridges formed times k_BT.

Because the bridging attraction is only of order k_BT per bridge, while the chain stretching and monomer interactions are many k_BT in a strongly-stretched brush, we expect that bridging will lead to only small perturbations of the self-consistent potential that obtains for interacting brushes in which only loops are permitted. We expect a brush of strongly-stretched loops to be essentially equivalent to a brush of half-chains with the same mass per unit area. The self-consistent potential $w\phi(z)$ of a brush of loops should be essentially the same as for the corresponding reference brush. The density of loop midpoints, denoted in this paper by $\epsilon(z)$, should be essentially the same as the free-end density in the corresponding reference brush.

To estimate the fraction of bridges, we need the Boltzmann weights $B_b(z)$ for telechelic chains forming bridges with midpoint at z. Since a telechelic chain is composed of two half-chains, the Boltzmann factor is the product of Boltzmann factors $A_L(z)$ and $A_R(z)$ (by symmetry, $A_R(z) = A_L(d - z)$ for surfaces separated by d) for the left and right half-chain. The Boltzmann factor $B_l(z)$ for loops (on the left surface, say) with midpoint at z is the square of the Boltzmann factor $A_L(z)$ for one of the two identical half-chains forming the loop. Since the Boltzmann factor for loops $B_l(z)$ is also proportional to the loop midpoint density $\epsilon_L(z)$, the Boltzmann factor for half-chains $A_L(z)$ must be proportional to $(\epsilon_L(z))^{1/2}$.

For brushes close enough to interact, the left- and right-hand loop midpoint density profiles $\epsilon_L(z)$ and $\epsilon_R(z)$, and hence the Boltzmann factors $A_L(z)$ and $A_R(z)$, overlap in a region of width ξ midway between the two surfaces. Thus the midpoints of bridges will be found in this region; the total number of bridges will scale as $\xi A_L(d/2 - h) A_R(d/2 - h) = \xi A_L(d/2 - h)^2 \propto \xi\epsilon(d/2 - h)$.

Consider two telechelic brushes brought into "classical contact", i.e., the surface separation is just large enough to accommodate the height of the brushes in the strong-stretching limit, so that their interaction is entirely mediated by the interpenetration and other fluctuation corrections to the strong-stretching limit. The number of bridges per unit area in this case should be given by the above estimate with d replaced by $2(h + \xi)$, or $\xi\epsilon(h + \xi)$.

Observe that the number of bridges is of the same order as the number of loop midpoints [density $\epsilon(h+\xi)$] in the overlap region (width ξ). In other words, in the overlap region there are a comparable number of midpoints belonging to loops and bridges. This is reasonable, since the Boltzmann weights must be comparable for loop and bridge configurations with midpoints located within ξ of the midplane between the two surfaces.

Since ξ is the length scale for fluctuation corrections to the midpoint density profile, we expect $\epsilon(h+\xi)$ may be estimated from the strong-stretching loop midpoint density at $h-\xi$. In marginal solvents the loop midpoint density is $\epsilon(z) = 3\sigma z h^{-3}(h^2 - z^2)^{1/2}$, which is of order $\sigma h^{-1}(\xi/h)^{1/2}$ for free-end positions z a distance ξ into the brush. Thus a fraction $(\xi/h)^{3/2}$ of chains will form bridges, and the bridging free energy per chain of brushes in classical contact is $kT(\xi/h)^{3/2}$.

Even if half the chains formed brushes, the attraction would never be more than kT per chain, whereas the free energy to compress a brush by a factor of 2 is of the order of the entire brush free energy $f_0 \sim \mu(0)N \sim (h/R)^2$, which is much greater than kT per chain for strongly-stretched brushes. Thus the interaction between telechelic brushes is certainly repulsive at short distances and may be attractive near or beyond classical contact.

Next, we describe the argument[19] leading to the penetration length ξ. Consider two reference brushes of half-chains compressed slightly into contact. In the strong-stretching limit, the chain conformations are dominated by those that locally balance chain tension and osmotic pressure gradients; fluctuations are small on the scale of the brush height h. In this limit, the osmotic pressure profile is a parabola in each brush, meeting in a cusp at the middle, and there is no interpenetration of chains from the two sides.

However, fluctuations lead to some interpenetration. To see this, we estimate the work required to pull the first s monomers at the free end of a chain on the right side past the cusp a distance l onto the left side. The chain stretches under tension as it is pulled into the higher-density region. The sum of stretching and additional interactions per chain may be estimated as $\Delta f = l^2/s + s\phi(0)l/h$.

If we choose the optimum length of chain $s(l)$ for a given interpenetration l and then assert that this interpenetration occurs by thermal fluctuations so that $\Delta f \sim kT$, we find a Boltzmann factor and thus an end density

$$\epsilon(z) \propto \exp[-C(l/\xi)^{3/2}] \tag{2}$$

with a penetration length defined by

$$\xi \equiv h(R/h)^{4/3} \tag{3}$$

The value of the coefficient C for brushes in classical contact turns out to be $C = 1.27\pi$ (see Appendix B). A similar argument, with thermal fluctuations pulling free ends beyond the extremity of a single brush, leads to a free-end density of the same functional form, with l replaced by $z-h$ and $C = \pi$.[19,20] In this case C is smaller because there is no osmotic pressure gradient resisting the fluctuation, but only the stretching penalty. Numerical calculations for two reference brushes at separations equal or greater than classical contact give end densities $\epsilon(z)$ in good agreement with these results (see Figure 1).

These results for interpenetration are slightly modified for brushes of loops. Because two half-chains must fluctuate simultaneously for a loop to extend beyond the edge of the brush or into an opposing brush, the work required for a given excursion is double, and the coefficient C is therefore replaced by $2C$.

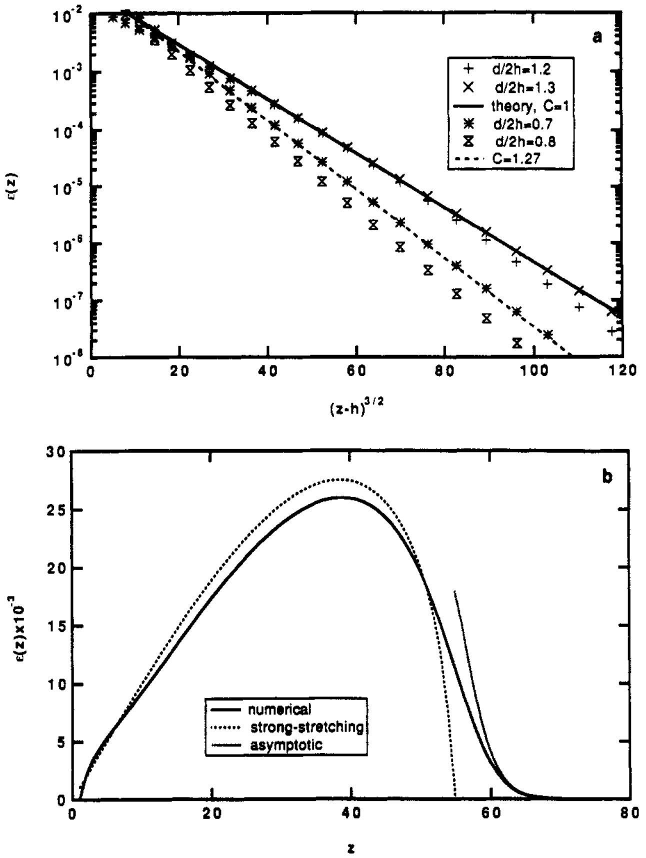

Figure 1. (a) The free-end density $\epsilon(z)$ follows an exponential decay law eq 2 for large excursions $z - h \gg \xi$ beyond the extrapolated outer limit of the brush. Shown are the asymptotic expression compared to the numerically obtained free-end density for one of two brushes at various surface separations d. For large brush separations $d - 2h \gg \xi$, the end density is well described by eq 2 with $C = \pi$; for brushes in compression ($d - 2h \ll \xi$), C takes the value 1.27π. (Here the chain length is $N = 150$ and the coverage is $\sigma = 0.04$.) (b) The asymptotic form of the free-end density of a single brush (dotted curve) is displayed together with the strong-stretching limit (dashed curve) and the numerically obtained self-consistent free-end density (solid curve) for $N = 200$, $\sigma = 0.04$.

We see that the penetration length ξ is the spatial dimension of that part of a penetrating chain with order kT of stretching and monomer interaction energy. When two brushes are brought into classical contact, it is only such fluctuations beyond the strong-stretching profile that lead to repulsions. That is, the repulsive interactions total about kT per penetrating chain for brushes in classical contact, which is the same order as the bridging attraction. Hence we expect the attractive minimum to be within ξ of classical contact.

To proceed more systematically, we introduce a single-chain partition function for telechelic chains

$$Z_s = \int Dz(s) \exp[-\mathcal{A}\{z(s)\}]$$

$$\mathcal{A}\{z(s)\} = \frac{3}{2}\int \mathrm{d}s \left(\frac{\mathrm{d}z}{\mathrm{d}s}\right)^2 + w\int \mathrm{d}s\, \phi(z(s)) \tag{4}$$

where $z(s)$ is a telechelic chain configuration with each of $z(1)$ and $z(2N)$ equal to either 0 or d (the locations of the two surfaces).

The partition sum may be broken up into three summands

$$Z_s = Z_s^{(L)} + Z_s^{(R)} + Z_s^{(b)} \tag{5}$$

according to which surface the end groups reside on; the three summands are respectively the sum of configurations for left-hand loops, right-hand loops, and bridges.

We may write each of the three summands as an integral over the midpoint positions of a product of further-restricted partition sums, which are precisely the partition sums of a half-chain in the potential $w\phi(z)$ with free end at z_N—in other words, the Boltzmann weights $A_L(z_N)$ and $A_R(z_N)$. For instance

$$\begin{aligned} Z_s^{(L)} &= \int \mathrm{d}z_N \int Dz(s)\, \delta(z(1))\, \delta(z(2N))\, \delta(z(N) - z_N) \times \\ &\qquad \exp[-\mathcal{A}\{z(s)\}] \\ &= \int \mathrm{d}z_N \left(\int_h Dz(s)\, \delta(z(1))\, \delta(z(N) - z_N) \times \right. \\ &\qquad \left. \exp[-\mathcal{A}_h\{z(s)\}]\right)^2 \\ &= \int dz_N\, [A_L(z_N)]^2 \end{aligned} \tag{6}$$

Here $\mathcal{A}_h\{z(s)\}$ is the action for a half-chain and $\int_h Dz(s)$ is the path integral over only half of the telechelic chain coordinates.

Similarly we may write

$$\begin{aligned} Z_s^{(b)} &= 2\int \mathrm{d}z_N\, A_L(z_N)\, A_R(z_N) \\ Z_s^{(R)} &= \int \mathrm{d}z_N\, [A_R(z_N)]^2 \end{aligned} \tag{7}$$

where $A_R(z)$ is the Boltzmann factor for right-hand half-chains. By symmetry, $Z_s^{(L)} = Z_s^{(R)}$. If bridging is forbidden, then we have only loop configurations and hence $Z_s^{(0)} = Z_s^{(L)} + Z_s^{(R)}$, but with in principle a different self-consistent monomer density profile than if bridging were allowed. The change in free energy per unit area $\Delta F(d)$ due to bridging between surfaces at separation d is then

$$\Delta F(d) = \sigma \log (Z_s/Z_s^{(0)}) \tag{8}$$

2. Large Separations

For large separations between the surfaces, we may assume that the self-consistent potential $w\phi(z)$, and hence the Boltzmann factors for half-chains of one brush, are unperturbed by the other brush. Thus the Boltzmann factors A_L and A_R for brushes well beyond classical contact may be taken from the results for an isolated brush of loops. Then the expression eq 8 for ΔF only includes attractive contributions, because the Boltzmann factors A_L and A_R appearing in Z_s and $Z_s^{(0)}$ are computed with the same self-consistent density profile.

The attractive free energy per unit area $W(d)$ due to bridging between surfaces at separation d is then

$$\begin{aligned} W(d) &= \sigma \log (Z_s/Z_s^{(0)}) = \sigma \log \Big[1 + \\ &\qquad \int \mathrm{d}z\, A_L(z)\, A_R(z) \left(\int \mathrm{d}z\, [A_L(z)]^2\right)^{-1}\Big] \approx \\ &\qquad \sigma \int \mathrm{d}z\, A_L(z)\, A_R(z) \left(\int \mathrm{d}z\, [A_L(z)]^2\right)^{-1} \end{aligned} \tag{9}$$

where the last approximation holds if the fraction of bridges is small. A first estimate of the repulsive interactions can be taken from eq 1 with the unperturbed density profiles from each brush. The dominant contribution to the integral in eq 9 for the attractive free energy comes over a small region near the midplane, where the concentrations of monomers from both surfaces are comparable, and $A_L \approx A_R$.

Well inside the brush, we have

$$A_L(z) \approx [h\epsilon_L(z)]^{1/2} \exp(-f_0) \tag{10}$$

where f_0 is the free energy per chain of the reference brush.

Well beyond the brush edge (at $z - h \gg \xi$), the argument from the work required to pull a half-chain out of the brush yields, as described in the previous section and Appendix B

$$A_L(z) \approx [C(\xi/h)^{1/2}]^{1/2} \exp(-f_0 - \pi((z - h)/\xi)^{3/2}) \tag{11}$$

The form of the prefactor has been chosen to match the previous result eq 10 at $z \approx h - \xi$ (the strong-stretching end density $h\epsilon(z) = 3z(h^2 - z^2)^{1/2}/h^2$ is of order $(\xi/h)^{1/2}$ a distance ξ into the brush). The scaling of this prefactor has been confirmed by numerical calculations of the kind described in the next section with various coverages σ and chain lengths N.

The constant prefactor may be determined by comparison to numerical results for the loop midpoint density in an isolated brush. We recall that $\epsilon(z) \propto A_L(z)^2$ and impose a normalization $\int \mathrm{d}z\, \epsilon(z) = 1$. The normalization integral is dominated by the classical region, whence $\int \mathrm{d}z\, A_L(z)^2 \approx \exp(-2f_0)$; thus we recover the well-known form[19,20,21]

$$\epsilon(z) \approx C\left(\frac{\xi}{h}\right)^{1/2} \exp[-2\pi((z - h)/\xi)^{3/2}] \tag{12}$$

Numerical results indicate $C \approx 2.5$.

The corresponding monomer density profile in isolated loop brushes for $z \gg h$ may be found from $\phi(z) = \int \mathrm{d}z'\, \epsilon(z')[\mathrm{d}z/\mathrm{d}n(z;z')]^{-1}$, which expresses the monomer density in terms of the contributions from chains passing through z. The chain tension $T = 3(\mathrm{d}z/\mathrm{d}n)$ in the most-extended half-chains is uniform beyond $z \approx h$. The tension T may be found by recalling that the exponent of the Boltzmann factor in eq 12 is the work required to pull an end to $z \gg h$. The tension is the derivative of the work, $T = 3\pi/2(z - h)^{1/2}\xi^{-3/2}$. This leads to the asymptotic form

$$\phi(z) \approx \frac{4C}{9\pi}\phi(0)\left(\frac{\xi}{h}\right) \exp\left[-2\pi\left(\frac{z - h}{\xi}\right)^{3/2}\right]\left(\frac{z - h}{\xi}\right)^{-1} \tag{13}$$

Again, the form of the prefactor is expected upon extrapolating to $z - h \approx \xi$ from the form of the strong-stretching density profile $\phi(z) = \phi(0)(1 - z^2/h^2)$ at a distance of order ξ inside the brush.

With these asymptotic forms for the monomer and free-end densities in the extremity of the brush of loops, we can evaluate the monomer–monomer interaction $V(d)$ and the bridging attraction $W(d)$ in the limit of widely-separated surfaces ($d \gg 2h$) using eqs 1 and 9. Anticipating that for widely-separated surfaces the monomer interactions will be dominated by the bridging attraction, we make a simple estimate of $V(d)$ using the overlapping unperturbed monomer densities of isolated loop brushes. Evaluating $V(d)$ by steepest descents, valid for $d - 2h \gg \xi$, leads to

$$\begin{aligned} V(d) &\approx w\phi^2(d/2)\xi\left(\frac{8(d - 2h)}{9\xi}\right)^{1/4} \\ W(d) &\approx \epsilon(d/2)\xi\left(\frac{(d - 2h)}{18\xi}\right)^{1/4} \end{aligned} \tag{14}$$

The narrow regions dominating the integrals for $V(d)$ and $W(d)$ in the limit of large separations between the surfaces have widths of order $\xi((d - 2h)/\xi)^{1/4}$ (which are much narrower than the separation $d - 2h$ between the brush extremities). The main dependence on d arises from the exponentially small factors of $\phi(d/2)^2$ and $\epsilon(d/2)$.

Because ϕ and ϵ have the same exponential decay, the bridging attraction $W(d) \sim \epsilon$ dominates the monomer repulsion $V(d) \sim \phi^2$ for $d \gg 2h$. This justifies our neglect of the monomer interactions in computing the Boltzmann factors $A_L(z)$ and $A_R(z)$ for well-separated brushes. Since bridging attraction dominates at large separations and monomer repulsions certainly dominate at small separations, we must have an attractive minimum. We expect this minimum to be located at $|d - 2h| \approx \xi$, as we shall now demonstrate.

The strong-stretching estimate of the free energy per chain of a brush under compression is[7,11]

$$f(\delta h) = {}^5/_9 f_0(1/u + u^2 - \mu^5/5) \qquad (15)$$

with $u = (h - \delta h)/h$ and f_0 may be written as $f_0 = (9\pi^2/40)(h/R)^2$. This leads to a repulsive energy per unit area which is third order in δh for small values (not second order, as one might expect from a simple quadratic minimum argument); at $\delta h \approx \xi$ this repulsive energy is of order $f_0\sigma(\xi/h)^3 \sim \sigma(R/h)^2$.

For $d - 2h \approx \xi$ both $V(d)$ and $W(d)$ are of order $\sigma(R/h)^2$. This follows for $W(d)$ directly from eqs 12 and 14 with $d - 2h \approx \xi$. For $V(d)$, using eqs 13 and 14 it suffices to note that $w\phi(0)^2h$ scales like the monomer repulsions and this is of the order of the brush free energy per unit area σf_0. Hence the location of the attractive minimum must be at $|z - h| \approx \xi$, since compression beyond this point leads rapidly to large repulsive forces.

We cannot employ the asymptotic forms for $V(d)$ and $W(d)$ in the vicinity of the minimum, but we can set $|d - 2h| \approx \xi$ to find the scaling of the depth of the minimum. Since both $V(d)$ and $W(d)$ are than of order $\sigma(R/h)^2$, the binding free energy per chain is of order $(R/h)^2$; this is much smaller than the free energy per chain of the reference brush, of order $(h/R)^2$, in the strong-stretching limit.

3. Numerical Results

To get more detailed information as to the shape of the interaction potential near the attractive minimum, including the precise depth and location of the well, we combine numerical self-consistent field (SCF) calculations with expressions 5–7 for the bridging attraction. We use a well-established algorithm developed by Scheutjens and Fleer[22,23] for solving SCF equations,[24,25] which contain a complete description of fluctuations of chain conformations about their classical paths, within the SCF approximation. We incorporate a low-density approximation (pairwise interactions of monomers) in the calculation, in accord with the assumptions of ref 11.

We determine the free energy and the monomer and midpoint densities as a function of the distance between the two brushes compressed together. Essentially, the numerical algorithm generates each of the three partition sums in eq 5 by using expressions 6 and 7, with the Boltzmann factors $A_L(z)$ and $A_R(z)$ generated by a transfer-matrix method proposed by Di Marzio and Rubin.[26]

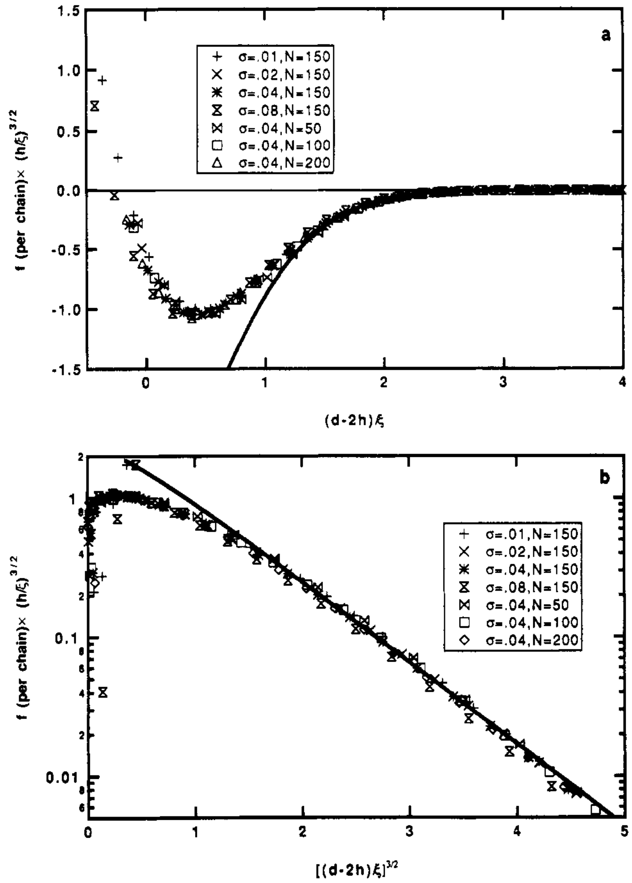

Figure 2. (a) The free energy per telechelic chain as a function of distance between surfaces d and a variety of half-chain lengths N (=50, 100, 150, 200) and half-chain coverages σ (=0.01, 0.02, 0.04, 0.08) can be collapsed onto a universal curve defined in eq 18. (b) The same data as in (a), plotted semilogarithmically versus $[(d - 2h)/\xi]^{3/2}$, show straight-line behavior at large surface separations.

The self-consistency condition is that the potential $w\phi(z)$ used in computing Boltzmann factors must be w times the expectation value of the density operator, which is

$$\langle\phi(z)\rangle = Z^{-1}\sigma\int_0^{2N} \mathrm{d}s\ [A_L(z;s)\ A_L(z;2N-s) + A_R(z;s)\ A_R(z;2N-s) + A_L(z;s)\ A_R(z;2N-s) + A_R(z;s)\ A_L(z;2N-s)] \qquad (16)$$

The first two terms correspond to the contribution of left-hand and right-hand loops, respectively; the last two terms (equal by symmetry) are the bridge contribution. Here $A_L(z;s)$ is the Boltzmann factor for a chain of s monomers attached to the left-hand surface with free end at z [with this notation, $A_L(z) = A_L(z;N)$].

As usual in self-consistent field calculations, the free energy per chain must be corrected from the single-chain partition function result by subtracting the doubly-counted monomer interactions. That is

$$\mathrm{f}(d) = -\log Z - w/(2\sigma)\int \mathrm{d}z\ [\phi(z)]^2 \qquad (17)$$

is the final result for the free energy per chain.

We obtain for various half-chain lengths N (=50, 100, 150, and 200 segments on a cubic lattice) and various numbers of half-chains per surface lattice site σ (=0.01, 0.02, 0.04, and 0.08) a set of curves for free energy per telechelic chain $\mathrm{f}(d)$ as a function of separation d between the surfaces (see Figure 2).

An example of the numerically calculated monomer, loop midpoint, and bridge midpoint density profiles at a surface separation corresponding to the attractive minimum is shown in Figure 3 for the case of chain length N = 150 and coverage σ = 0.04.

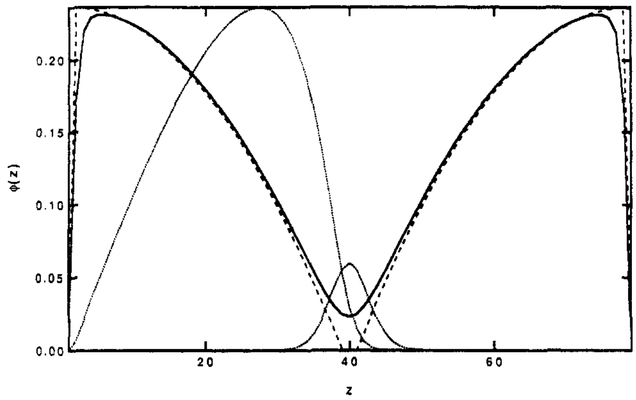

Figure 3. Shown are the total monomer density (solid curve), classical strong-stretching monomer density (dashed curve), and midpoint density for left-hand loops and bridges (dotted curves) for two brushes at a surface separation corresponding to the attractive minimum. (Here chain length $N = 150$ and coverage $\sigma = 0.04$.)

In the vicinity of the attractive minimum, the free energy curves scale as anticipated in the previous section:

$$f(d) \equiv (\xi/h)^{3/2}\,\tilde{f}[(d-2h)/\xi] \qquad (18)$$

defines a universal function $\tilde{f}(x)$ that collapses the numerical data. From the collapsed data, we can read off the depth f^* and position x^* of the attractive minimum in reduced units as $f^* \approx -1.0$ and $x^* \approx 0.4$, respectively.

The asymptotic result of eq 14 applies for separations where the tail of the loop midpoint density is well estimated as for a single brush of loops. We noted in the previous section (see Figure 1) that the numerical value of the penetration length depends on whether the brush is isolated or in contact with another brush. Starting with brushes in classical contact, as the separation between the surfaces is increased, the coefficient C in eq 2 decreases from 1.27π to π. This occurs in the vicinity of the attractive minimum of Figure 2. Thus the attractive interaction, which decays as the loop midpoint density, may decay over this range less slowly than the asymptotic result eq 14. A good fit to the attractive tail is obtained with the form implied by eq 13 for $\epsilon(z)$ and eq 14 for the attraction $W(d)$, with the exponent of eq 13 multiplied by 0.7.

4. Scaling in Good Solvents and Melts

It is straightforward to extend our scaling results for the fraction of bridges formed in brushes at classical contact, and the depth of the attractive minimum in the free energy per telechelic chain, for the two cases of good solvents and melts with homopolymer intervening between the brushes.

Consider two brushes in good solvent at classical contact. From previous work[11] we know that the free energy per chain in a slightly compressed good-solvent brush still scales as $f(h < h_0) \sim f_0[(h_0 - h)/h_0]^3$ (assuming the Flory value for $\upsilon = 3/(d+2)$ in d dimensions), just as for marginal solvents. We set $h_0 - h = \xi$ for classical contact and recall that in the scaling picture the free energy per chain is kT times the number of blobs, h/ξ_0. Here ξ_0 is the distance between attachment points on the surface; $1/\xi_0^{(d-1)}$ is the number of chains per $(d-1)$-dimensional "area".

On the other hand, we observe that the penetrating segments must be at overlap concentration so as to have kT of interaction energy each. (As we argued in section 1, the bridging attraction at classical contact is also of the order of kT per penetrating chain.) Hence two equivalent ways of writing the repulsions at classical contact are

$$(h/\xi_0)(\xi/h)^3(1/\xi_0^{(d-1)}) \sim 1/\xi^{(d-1)}$$

which leads to $\xi/h \sim (\xi_0/h)^{d/(d+2)}$. We replace the chain separation ξ_0 in terms of the swollen radius $R^D \sim N$ ($D \equiv 1/\upsilon$) by writing the monomer density in two different ways

$$N/(h\xi_0^{(d-1)}) \sim \xi_0^D/\xi^d$$

which gives $\xi_0/h \sim (R/h)^{D/(D-1)}$. Hence we have finally (using the Flory υ)

$$\xi/h \sim (R/h)^{dD/[(d+2)(D-1)]} = (R/h)^{d/(d-1)}$$

For $d = 4$ we recover the marginal solvent exponent $d/(d-1) = {}^4/_3$ of ref 19; for $d = 3$ dimensions we have the exponent $d/(d-1) = {}^3/_2$. The corresponding scale of repulsive and attractive free energies per chain and fraction of bridges all scale as $(\xi_0/\xi)^{d-1} \sim (R/h)^{2D(d-1)/[(D-1)(d+2)]} = (R/h)^2$, independent of dimension, with the Flory value for D.

Our approach for taking into account the effects of bridging may also be applied to brushes under melt conditions. This situation has been studied recently by Halperin and Zhulina.[27] Consider the chain conformations in strongly-segregated A–B multiblock lamellar mesophases. Here, the junctions between consecutive A and B blocks are strongly localized on narrow interfaces between nearly pure components; and the chains in the A and B domains are stretched to some degree. The question arises in a multiblock system how frequently a single A block bridges the entire A domain and how often it forms a loop, extending only halfway into the domain. This is relevant to a variety of rheological and mechanical properties.

We repeat the argument of the previous section to estimate the fraction of bridges. Note that for strongly-segregated melt brushes, the end density is $\epsilon(z) = \sigma z h^{-1}(h^2 - z^2)^{-1/2}$, while the penetration depth still satisfies eq 3 because the potential remains parabolic. The fraction of bridges under melt conditions then becomes[27] $\sigma^{-1}\epsilon(\xi)(\xi/h) \sim (\xi/h)^{1/2} \sim (R/h)^{2/3}$. The greater tendency in reference melt brushes for half-chain free ends to be close to the outer extremity leads to a larger fraction of bridges.

With this result, we may consider the interactions of two melt brushes formed of telechelic chains and separated by intervening long homopolymers. The brushes may be brought into contact by expelling the homopolymer. When the brushes come into classical contact, we again expect that repulsions and attractions mediated by interpenetrating and bridging chains are of order kT per interpenetrating chain. As before, these are of the same order because the overlap zone is essentially defined so that the interpenetrating portions of the chain have kT of interaction energy, and the bridging attraction is roughly kT per half-chain end in the overlap zone. For more separated melt telechelic brushes, we expect residual attractions to dominate as in the previous section; hence we expect an attractive minimum for melt telechelic brushes near classical contact with a depth of order $(R/h)^{2/3}$ per chain.

5. Discussion

The preceding calculations have shown, and we have argued quite generally, that the attractive interactions between surfaces induced by telechelic chains (polymers with an adsorbing group at each end) can never exceed of order kT per chain in equilibrium. The basic reason for this is that the bridging attraction is driven by the entropy gained when a chain with a given midpoint location is free to choose the paths of its two arms so as to form a bridge or a loop on either surface.

This decrease in free energy can never be more than kT per chain; and it may be considerably less, averaged over all chains in the brush, if most chains are obliged because of the strong stretching to form loops. This manifests itself within our scheme of computing the Boltzmann factors of loops or bridges as the product of Boltzmann factors for the corresponding pair of half-chains, in that the half-chain Boltzmann factors, or equivalently the density of half-chain free ends to be joined from the left and right surfaces, do not overlap much.

The binding energy of the adsorbing "sticker" group does not drive the formation of bridges, because the stickers can bind to either surface; two separated brushes of loops can completely satisfy the stickers. If the stickers on the two ends of the chain are different and have unequal affinities for two different surfaces, bridging can be driven by the sticker energy. An example is the bridging problem considered by Johner and Joanny,[28] in which the free ends of a permanently grafted brush were assumed to bind with some energy only to a second, initially bare surface. In this case, the sticker binding energy drives the formation of a substantial number of bridges; when the binding energy is equal to the difference in free energy per chain between a self-consistent brush and the uniformly stretched "step-function" ansatz, all of the chains bridge the two surfaces, and a step-function brush is produced.

Even though the attractive energy per chain $(R/h)^2$ is much smaller than kT for strongly-stretched brushes of telechelic chains, this can give reasonably large binding energies between large colloidal particles. Two colloidal particles of diameter D with telechelic brushes of height $h \ll D$ adsorbed on their surfaces and placed in near-contact (separated by $\approx 2h$) will have a "footprint" area of attractive contact A of order $D\xi$. The binding free energy per area ΔF will be of order $(R/h)^2\sigma$, and the total binding free energy $A\Delta F$ of order $(DR\sigma)(R/h)^{7/3}$. For micron-sized particles, a stretch ratio $h/R \approx 5$, a coverage $\sigma \approx (50\ \text{Å})^{-2}$, and chains of moderate size ($R \approx 100$ Å), the total binding free energy due to bridging is about $10kT$.

Bridging attractions like those seen here occur in bulk solutions of associating polymers, such as ionomers.[29] Here the associating groups assemble into well-defined micelles. It has been argued that these micelles must experience a net mutual attraction due to bridging,[30] if the number of associating groups in a micelle is large. The present results corroborate this conclusion; even the strong repulsion expected between the micelle cores does not prevent a net attraction when the micelles just touch.

The discussion up to this point has presumed an equilibrium situation, in which the adsorbing groups are free to exchange between the two surfaces. (We have for simplicity considered a restricted equilibrium in which the total number of chains per unit area remains fixed; however, this is not an essential restriction, since the coverage of separated brushes is determined by the equilibrium with the solution, and the bridging attraction is weak enough that the equilibrium coverage is little perturbed.) This is appropriate for considering, e.g., the thermodynamic stability of colloids with telechelic brushes.

However, for considering experiments using the surface forces apparatus, a variety of nonequilibrium effects may be important. Foremost among these is that the exchange of the adsorbing groups between surfaces may take a long time, especially if the sticker binding energy is large. Entanglement effects between the telechelic chains in loop configurations on the same or opposite surfaces may also be important. One way in which such kinetic effects may be probed is to incubate the telechelic chains between surfaces under one set of conditions and then quickly make a force measurement.

For example, surface held at a separation of order R in the presence of a concentrated solution of telechelics may form many bridges, because stretching energy is not relevant under these conditions. This behavior can be seen within the picture of loop and bridge formation from brushes of half-chains in the following way. As two brushes are strongly compressed together, the cusp in the monomer density implied by the fluctuation-free strong-stretching theory becomes less sharp; the monomer density becomes uniform, and the stretching energy decreases. This makes interpenetration easier; the chain end pulled by thermal fluctuations from one brush across the cusp onto the other side sees both less osmotic pressure gradient and less stretching penalty. The width of the overlap region, in which loop midpoints from each surface freely mix and bridge midpoints are equally likely, grows as the brushes are compressed.

Thus the fraction of bridges in restricted equilibrium (fixed total coverage) should rise smoothly under compression, from a small fraction of order $(R/h)^2$ at weak compression to one-half for strongly compressed brushes. Telechelic brushes between surfaces so prepared may then have an adjustable fraction of bridges; then the calculation of Ligoure et al.[15] may be relevant for determining the force versus distance between surfaces if the adsorbing groups are effectively immobile during the experiment.

We may summarize our simple argument for the fraction of bridges at weak compression as follows. The region of overlap, in which the midpoints of chains are equally likely to be in bridges or loops, is of relative width ξ/h. The loop midpoint density profile in the strong-stretching limit is the same as the free-end density in a reference brush of half-chains and vanishes with a square-root dependence at the outer limit of the brush. Hence the fraction of chains forming bridges should be order ξ/h times the characteristic scale $(\xi/h)^{1/2}$ of the loop midpoint density in the overlap region, giving a fraction of bridges $(\xi/h)^{3/2} \sim (R/h)^2$. The fraction of bridges at classical contact also scales as $(R/h)^2$ in telechelic brushes under good solvent conditions, as shown in section 4, when the Flory value for v is taken. This agreement between brush exponents for marginal and good solvent cases also appears, e.g., in the height scaling relation $h \sim N\sigma^{1/3}$, which holds in both cases.

Finally, the present approach of estimating the number of loops and bridges may be employed to describe effects of bridging in telechelic brushes under melt conditions. Strongly-segregated A–B multiblock lamellar phases may be viewed as constructed by joining free ends in a reference state of A–B diblocks. Bridging then corresponds to blocks that span an entire domain rather than looping back to the same A–B interface. The above simple argument for the fraction of bridges is modified because the loop midpoint density a distance ξ inside a melt brush of loops is of relative order $(\xi/h)^{-1/2}$. This results in a fraction of bridges scaling as $(\xi/h)^{1/2} \sim (R/h)^{2/3}$ in strongly-stretched telechelic melt brushes.

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Appendix A

Here we show that when the ends of telechelic chains are strongly adsorbing, so that the resulting brush is strongly stretched, few of the chains are attached by a single end. Consider a single surface in equilibrium with a solution of telechelic chains at concentration ϕ. If the stretching and monomer interaction ("brush") free energy of the last half-chain added is f and the sticker binding energy is ΔE, the equilibrium for loop adsorption from solution is[31]

$$T \log (\sigma/2) + 2(f - \Delta E) = T \log \phi \qquad (19)$$

(The first term is the entropy of mixing for the adsorbed loops; recall the coverage of telechelic chains on each surface is $\sigma/2$.)

In this context we may regard the singly attached chains or "tails" as a grafted chain of twice the length of each half-chain in a loop. The brush free energy to add such a chain of length $2N$ is in general greater than that required to add a half-chain of length N, because of the additional stretching and monomer interaction penalty paid by the additional N monomers.

Detailed calculations in the strong-stretching limit[32] show that the cost to add the last chain of length $N_t = 2N$ to the brush is $f(1 + \phi_l^{2/3})$, where ϕ_l is the fraction of tails adsorbed. Hence the equilibrium for tails is

$$T \log (\sigma\phi_t) + f(1 + \phi_l^{2/3}) - \Delta E = T \log \phi \qquad (20)$$

Comparison of eqs 19 and 20 leads to

$$T \log \phi_t + f\phi_t^{2/3} = {}^1\!/_2 T \log (2\phi/\sigma) \qquad (21)$$

If the solution concentration is rather small, the first and third terms of eq 21 balance at a small value of the tail fraction ϕ_t, for which the second term is negligible; this leads to $\phi_t \sim (\phi/\sigma)^{1/2}$. If the solution concentration is reasonably high, tail chains will attach until the extra penalty (second term) balances the in-plane entropy of mixing; this leads to $\phi_t \sim (f/T)^{3/2} \sim (R/h)^3$, which is small for strongly stretched brushes. In either case, the fraction of singly-attached chains may be neglected.

Appendix B

Here we review and extend the calculations of refs 19 and 20 for the work required to pull a chain end out of a brush a distance l beyond the brush edge to the case of pulling the chain end into a second brush pressed against the first, against osmotic pressure. The exponential of the work required gives the Boltzmann factor for the probability of an end making such an excursion.

The "classical" trajectory of a chain under tension, with its free end pulled beyond the edge of its brush to a location $z = h + l$, satisfies the equation of motion

$$\frac{\mathrm{d}^2 z}{\mathrm{d}n^2} = -\frac{\mathrm{d}U}{\mathrm{d}z} \qquad (22)$$

where $U(z) = -w\phi(z)/3$ is defined so that eq 22 takes the form of the motion of a particle in a potential $U(z)$. The trajectory takes different forms within the region where U is parabolic $[U = \pi^2/(8N^2)(h^2 - z^2)]$ and beyond the brush edge where U is linear $[U = \mathrm{d}U/\mathrm{d}z(z - h)]$. The trajectory beyond the cusp is

$$z(n) = h + l - \upsilon(0)n + \frac{1}{2}\frac{\mathrm{d}U}{\mathrm{d}z}n^2 \qquad (23)$$

The chain is under tension, which corresponds to $\mathrm{d}z/\mathrm{d}n = \upsilon(0) \neq 0$. (The free end corresponds to $n = 0$.) Suppose fN monomers have been pulled beyond the brush edge; then $z(fN) = h$, which implies

$$\upsilon(0) = \frac{l}{fN} + \frac{1}{2}\frac{\mathrm{d}U}{\mathrm{d}z}fN \qquad (24)$$

Inside the brush where u is parabolic, $z(n)$ is given by

$$z(n) = h \cos (\pi n/(2N))/\cos (\pi f/2) \qquad (25)$$

which satisfies the equation of motion eq 22 and $z(fN) = h$. The chain tension must be continuous across the brush edge, which implies

$$\upsilon(0) = \frac{\pi h}{2N} \tan (\pi f/2) + \frac{\mathrm{d}U}{\mathrm{d}z}fN \qquad (26)$$

Equations 24 and 26 can be used to eliminate $\upsilon(0)$ and find a relation between l/h and f.

The chain free energy, or minimum work required to pull the end to $z = h + l$, is evaluated directly from the general expression

$$f = \int \mathrm{d}n \left[\frac{3}{2}\left(\frac{\mathrm{d}z}{\mathrm{d}n}\right)^2 + w\phi(z(n))\right] \qquad (27)$$

Using the trajectories eqs 23 and 25, eqs 24 and 26 to eliminate $\upsilon(0)$, and the assumption $f \ll 1$ that a small fraction of the monomers are pulled out of the brush, we obtain after some algebra

$$f = f_0 + C(\gamma)(l/\xi)^{3/2}$$

$$C(\gamma) = \pi(1 + 2\gamma + {}^4\!/_3\gamma^2)(1 + \gamma)^{-3/2} \qquad (28)$$

where $\gamma \equiv 2N^2/(h\pi^2)\,\mathrm{d}U/\mathrm{d}z$, $\xi \equiv h(R/h)^{4/3}$, and f_0 is the free energy of a nonpenetrating chain. The probability of the penetration fluctuations is then proportional to $\exp[-(f - f_0)]$.

For penetration of chain free ends beyond the brush edge into solvent, $\gamma = 0$ and we recover $C(0) = \pi$. For the case of penetration of chains from one brush into another brush brought into classical contact, $\mathrm{d}U/\mathrm{d}z = \pi^2 h/(4N^2)$ and $\gamma = {}^1\!/_2$, which gives $C(\gamma) = 1.270$.

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