Inducing and Measuring Bridging in Telechelic Polymer Brushes

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ABSTRACT: We investigate bridging in a telechelic polymer brush in solution using the Milner−Witten−Cates self-consistent mean-field model. For an uncompressed brush between flat, parallel plates, the equilibrium number of bridges is predicted to be proportional to $(R/L_0)^2$, where R is the root-mean-square end-to-end distance and L_0 is the equilibrium brush height. Upon compressing this system, a much higher number of bridges form. For moderate compression $L_0 - L$ such that $\xi \ll L_0 - L \lesssim L_0/2$, where ξ is the interpenetration depth between two opposing brushes, the number of bridges is proportional to $(L_0 - L)(R/L_0)^{2/3}$. Changing the geometry of the system from flat, parallel plates to crossed cylinders changes the way the number of bridges scales with compression distance. In the crossed cylinder configuration, under moderate compression M such that $\xi \ll M \lesssim L_0/2$, the number of bridges is proportional to $M^2(R/L_0)^{2/3}$. If the two surfaces are pulled apart with a fixed number of bridges, the tensile force is approximately proportional to the number of bridges, for both the parallel plate configuration and the crossed cylinder configuration.

I. Introduction

Polymer brushes are formed when polymer chains are tethered by one or both ends to a surface or interface at a sufficiently high density that the chains stretch away from the interface. Examples of such brushes arise in a variety of contexts. Colloidal suspensions are often stabilized by attaching end-grafted chains. Polymer brushes are also useful in understanding block copolymers.[1−3]

Polymer brushes in which each chain has one end tethered to an interface have been studied extensively, both experimentally[4−6] and theoretically.[7−12] Less work has been done on polymer brushes consisting of telechelic chains (linear chains with "stickers" at both ends). A telechelic chain can form a loop, in which both ends are attached to the same interface, or (if a second interface is nearby) a bridge, in which the two ends are attached to different interfaces. Loops can be easily described by the theory developed for singly tethered chains by taking advantage of the correspondence between the loop midpoint of a doubly tethered chain and the free end of a singly tethered chain. Bridges, on the other hand, introduce new properties. Consider two surfaces with bridging chains connecting the surfaces. These bridges do not significantly perturb the force versus distance profile when a force compressing the two surfaces together is applied. But when an extensional force is applied, the bridges resist this extensional force; such a resisting force cannot occur in brushes consisting of singly tethered chains. The effects of bridging have been studied in a variety of systems, including strongly stretched polymer melts,[13−15] strongly stretched polymer brushes in solution,[16−21] nearly Gaussian polymers in solution,[22,23] charged polymer brushes,[24,25] and liquid crystalline polymers.[26,27] In this paper, we focus on strongly stretched polymer brushes in solution. The pioneering experimental studies of Dai and Toprakcioglu[28,29] showed that the bridging of telechelic chains between surfaces immersed in solvent can produce substantial attraction. However, most of this attraction disappears as the chains relax to equilibrium. Indeed, equilibrium telechelic polymer brushes in solution are expected to have little bridging on theoretical grounds.[19] In this paper, we suggest a method for preparing a controlled number of bridges and a procedure for measuring the number of bridges using the surface forces apparatus.[5,6,30−32]

Our bridged brush system consists of two surfaces and telechelic chains. Each telechelic chain is $2N$ monomers long and has stickers at both ends. We assume that the attraction between surface and sticker is sufficiently strong such that there are practically no free ends but not strong enough to permanently (irreversibly) attach the sticker to the surface. In the next section, we introduce a reference, unbridged brush consisting of singly grafted half-chains. In section III, we infer the properties of the telechelic brush from the properties of the reference brush, first for a single surface, then for two nearby surfaces. We show how to make a controlled number of bridges in a system with telechelic chains attached to flat, parallel surfaces. In section IV, we suggest a method for measuring the number of bridges by applying normal forces to the bridged brush. In section V, our results are extended to the crossed cylinder configuration. We discuss the implications of our work in the final section.

II. Properties of Singly Grafted Chains

It is convenient to introduce a reference system of singly grafted half-chains. Each half-chain is N monomers long and has one sticker end and one free end. The characteristics of singly grafted chains have been studied extensively. When the grafting density is sufficiently high so that the average distance between grafting sites is much less than the radius of gyration of the polymers, the polymers become strongly stretched. The height of the brush is determined by the balance between two opposite effects—the excluded volume interaction and entropic effects. The excluded volume energy scales as $\int dV\ v\phi^2 \sim v\sigma N^2/L$, where dV is a volume element, v is the pairwise excluded volume parameter, ϕ is the monomer concentration, σ is the grafting density, and L is the brush heigh; the excluded volume energy decreases with increasing brush height. The free energy of stretching a chain to a height L larger than the root-mean-square end-to-end distance R scales as $(L/R)^2$; this stretching free energy increases with increasing height. In the limit of long chains, high grafting density, and marginal solvent quality, Milner,

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Witten, and Cates (MWC) have proposed an analytic self-consistent mean-field theory.[8,9] In this limit, fluctuations about the most probable paths are not important, and the partition function is dominated by the "classical" paths of the chains. In this classical, fluctuation-free limit, the height of an equilibrium (uncompressed) brush is

$$L_0 = \left(\frac{12}{\pi^2}\right)^{1/3} N\sigma^{1/3} v^{1/3} a^{2/3} \quad (1)$$

where a is the effective monomer length. The concentration profile of a brush (possibly) compressed to a height $L \le L_0$ is

$$\phi(z) = \frac{A}{v} - \frac{B}{v} z^2 \quad (2)$$

where z is the distance from the surface,

$$B = \frac{\pi^2}{8N^2 a^2} \quad (3)$$

and

$$A = \frac{N\sigma v}{L} + \frac{BL^2}{3} \quad (4)$$

The density of chain free ends is

$$\epsilon(z) = \frac{B}{Nv}\left[2z\,(L^2 - z^2)^{1/2} + \left(\frac{A}{B} - L^2\right) z (L^2 - z^2)^{-1/2}\right] \quad (5)$$

$$= \left(\frac{\sigma}{L}\right)\left(\frac{z}{L}\right)\left\{3\left(\frac{L}{L_0}\right)^3\left[1 - \left(\frac{z}{L}\right)^2\right]^{1/2} + \left[1 - \left(\frac{L}{L_0}\right)^3\right]\left[1 - \left(\frac{z}{L}\right)^2\right]^{-1/2}\right\} \quad (6)$$

When $L = L_0$ (that is, no compression), eq 6 reduces to

$$\epsilon_0(z) = 3\left(\frac{\sigma}{L_0}\right)\left(\frac{z}{L_0}\right)\left[1 - \left(\frac{z}{L_0}\right)^2\right]^{1/2} \quad (7)$$

III. Telechelic Chains on Flat Surfaces

To establish the relationship between one-sticker half-chains and telechelic (two-sticker) chains, we first consider a system consisting of telechelic chains attached to one surface. Because of the strong attraction between surface and sticker, all of the telechelic chains form loops. The midpoint of a loop corresponds to the free end of a singly grafted chain, and the properties of a brush consisting of loops are readily related to the properties of a brush consisting of singly grafted chains. The telechelic brush may be constructed from the half-chain brush by joining each free end to another at the same height z. In the strongly stretched limit, this joining process has little effect on the stretching profile of each chain or the position of its (original) end.[19] Thus, the density of loop midpoints $\epsilon_L(z)$ for a brush consisting of loops is equal to half the density of free ends $\epsilon(z)$ for a brush consisting of singly grafted chains, and the concentration profile $\phi_L(z)$ for a brush made up of loops is identical to the concentration profile $\phi(z)$ for a brush made up of singly grafted chains.

We now consider a system consisting of telechelic chains attached to two flat, parallel surfaces separated by the distance $2L$. The equilibrium separation $2L$ is approximately $2L_0$. At this separation, a small number of bridges form. The number of bridges can be estimated by looking at the interpenetration between two reference brushes (each of height L_0) consisting of singly grafted half-chains. In a completely fluctuation-free system, no interpenetration between the two brushes would occur. However, fluctuations on the order of kT per chain allow chains from one brush to penetrate into the opposite brush. Witten, Leibler, and Pincus[33] have estimated the free energy required to stretch a chain from L_0 to $L_0 + \xi_0$, where $\xi_0 \ll L_0$.

$$\frac{\Delta F_0}{kT} \approx \left(\frac{L_0}{R}\right)^2\left(\frac{\xi_0}{L_0}\right)^{3/2} \quad (8)$$

where $R = N^{1/2}a$ is the root-mean-square end-to-end distance of a free, ideal chain of length N in solution and prefactors on the order of unity have been omitted.

To understand qualitatively how eq 8 arises, we estimate the free energy required for a free polymer end to penetrate a depth ξ_0 into a polymer brush of height L_0. Let P be the number of monomers of the free polymer that penetrate into the brush. The potential energy required for P monomers to penetrate into a brush up to a depth of ξ_0 is $Pv\phi(L_0 - \xi_0) \approx PBL_0\xi_0 \approx (PL_0\xi_0)/(N^2a^2)$, where prefactors on the order of unity have been omitted. The stretching energy required to stretch P monomers a distance ξ_0 is, omitting numerical prefactors, $\xi_0^2/(Pa^2)$. Minimizing the sum of the potential and stretching energies yields $P = (\xi_0/L_0)^{1/2}N$, and thus the total free energy scales as $(L_0/R)^2(\xi_0/L_0)^{3/2}$, as in eq 8. Changing the problem from the free energy required for a free polymer end to penetrate a brush to the free energy required for a brush to penetrate an opposing brush does not change the scaling of the free energy with ξ_0 and L_0, as is rigorously demonstrated in ref 33.

By setting $\Delta F_0/(kT)$ to 1 in eq 8, the penetration depth ξ_0 into a polymer brush by the opposite brush is estimated to be

$$\frac{\xi_0}{L_0} \approx \left(\frac{R}{L_0}\right)^{4/3} \quad (9)$$

where numerical prefactors have been omitted. The fraction γ_0 of chain ends of the reference brush in the interpenetration zone is found by integration.

$$\gamma_0 \approx \frac{\int_{L_0-\xi_0}^{L_0} \mathrm{d}z\ \epsilon_0(z)}{\int_0^{L_0} \mathrm{d}z\ \epsilon_0(z)} \approx \left(\frac{\xi_0}{L_0}\right)^{3/2} \approx \left(\frac{R}{L_0}\right)^2 \quad (10)$$

where, again, numerical prefactors have been omitted. In deriving this result, it is assumed that $\xi_0 \ll L_0$, which is consistent with our use of the classical MWC self-consistent mean-field theory. If this assumption were not true, it would inappropriate to use the MWC theory.

We return to the system of telechelic chains and two surfaces. If the chains were prevented from forming bridges, the fraction of loop midpoints in the interpenetration zone would be approximately γ_0. When the chains are allowed to form bridges, the equilibrium number of bridges is proportional to the fraction γ_0 of loop midpoints in the interpenetration zone. Thus, the equilibrium bridging fraction for telechelic chains attached to two surfaces is

$$\eta_0 \approx \left(\frac{\xi_0}{L_0}\right)^{3/2} \approx \left(\frac{R}{L_0}\right)^2 \quad (11)$$

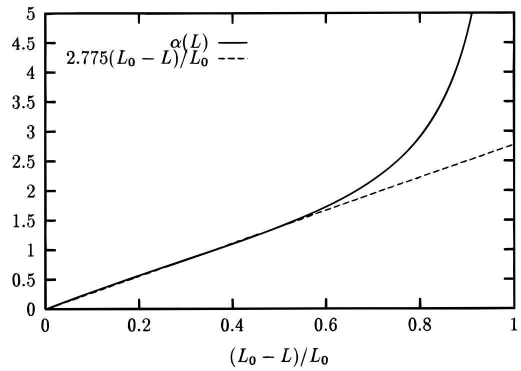

Figure 1. $\alpha(L)$, as defined in eqs 14 and 15, versus compression factor $(L_0 - L)/L_0$. We note that $\alpha(L)$ is approximately linear in $(L_0 - L)/L_0$ over the range $0 \le (L_0 - L)/L_0 \lesssim 0.5$.

where prefactors on the order of unity have been omitted. This result is consistent with ref 19.

A bridging fraction η much larger than η_0 can also be achieved by compressing the two surfaces together to a separation of $2L < 2L_0$ and allowing the system to reach equilibrium under compression. In practice, the system may require a long time to reach equilibrium due to the large free energy barrier between loops and bridges. When the compression is released, the bridges are slow to convert to loops, resulting in a long-lived nonequilibrium state with a high bridging fraction η.

Proceeding similarly as above, the bridging fraction attained under compression can be estimated by looking at the interpenetration zone of two reference brushes (each compressed to height L) consisting of singly grafted half-chains. The free energy required to stretch a chain from L to $L + \xi$ (where $\xi \ll L$) is

$$\frac{\Delta F}{kT} \approx \left(\frac{L}{R}\right)^2 \left(\frac{\xi}{L}\right)^{3/2} \tag{12}$$

The penetration depth ξ is

$$\frac{\xi}{L} \approx \left(\frac{R}{L}\right)^{4/3} \tag{13}$$

where prefactors on the order of unity have been omitted. The fraction γ of chain ends of the reference brush in the interpenetration zone is found to be

$$\gamma \approx \frac{\int_{L-\xi}^{L} \mathrm{d}z\, \epsilon(z)}{\int_0^L \mathrm{d}z\, \epsilon(z)} \approx c_1\left(\frac{L}{L_0}\right)\left(\frac{R}{L_0}\right)^2 + c_2\alpha(L)\left(\frac{R}{L_0}\right)^{2/3} \tag{14}$$

where

$$\alpha(L) = \left(\frac{L}{L_0}\right)^{-2/3}\left[1 - \left(\frac{L}{L_0}\right)^3\right] \tag{15}$$

and c_1 and c_2 are constants of the order unity. In deriving this result, it is assumed that $\xi \ll L$.

For a system consisting of telechelic chains attached to two surfaces, the bridging fraction η is proportional to γ for the corresponding reference system of singly grafted chains. Thus,

$$\eta \approx c_3\left(\frac{L}{L_0}\right)\left(\frac{R}{L_0}\right)^2 + c_4\alpha(L)\left(\frac{R}{L_0}\right)^{2/3} \tag{16}$$

where c_3 and c_4 are constants of the order unity. $\alpha(L)$ is nearly proportional to $(L_0 - L)/L_0$ for a large range of moderate compression. Figure 1 shows that $\alpha(L) \approx 2.775(L_0 - L)/L_0$ over the range $0 \le L_0 - L \lesssim L_0/2$. Thus, for moderate compression, eq 16 simplifies to

$$\eta \approx c_5\left(\frac{L}{L_0}\right)\left(\frac{R}{L_0}\right)^2 + c_6\left(\frac{L_0 - L}{L_0}\right)\left(\frac{R}{L_0}\right)^{2/3} = \left(\frac{L}{L_0}\right)\eta_0 + c_6\left(\frac{L_0 - L}{L_0}\right)\left(\frac{R}{L_0}\right)^{2/3} \tag{17}$$

where c_5 and c_6 are constants of the order unity. The restriction to moderate compression is not a serious shortcoming. For very strong compression, the brush height L would become comparable to the mean-square end-to-end distance R, and the MWC self-consistent mean-field theory (which all of our calculations are based on) would no longer be valid.

When $L_0 - L \gg \xi$—that is, when the brush is compressed by a distance much greater than the interpenetration depth—the first term in eq 17 becomes negligible, and the expression for the bridging fraction η further simplifies to

$$\eta \approx c_6\left(\frac{L_0 - L}{L_0}\right)\left(\frac{R}{L_0}\right)^{2/3} \tag{18}$$

This result is valid for the compression range $\xi \ll L_0 - L \lesssim L_0/2$.

By varying the amount of compression $L_0 - L$, the bridging fraction η can be easily controlled. Comparing eqs 11 and 18, we see that the bridging fraction η resulting from compression can be much larger than the equilibrium bridging fraction η_0 under no compression.

IV. Applying Normal Forces to the Bridged Brush

In this section, we show how to determine the bridging fraction by applying normal forces to the bridged brush. We assume that the normal force measurements described below can be performed quickly enough that the bridging fraction does not change appreciably during the measurements. Over a short period of time, the high free energy barrier between bridges and loops keeps the bridging fraction η essentially constant. The assumption here of constant η is in direct contrast to that of the previous section, where the system is incubated for a long time until η has reached its equilibrium value.

When a strong compression force is applied to the bridged brush, the force is nearly independent of the bridging fraction η. In this limit, the excluded volume interaction dominates, and the effects of loops and bridges are essentially the same. When a strong pulling force is applied to the system, the force is approximately proportional to the bridging fraction η. In this limit, only the chain tension of the bridges resists the pulling force. In between these two limits, the excluded volume interaction of both loops and bridges together with the chain tension of the bridges combine to yield a more complicated relationship between force and bridging fraction.

A method for determining the bridging fraction η would be to measure f_T, the tensile normal force per unit area, at a large surface separation $2L_T$ such that the bridged brush is highly extended; in this region, f_T is approximately proportional to η.

$$f_T = \tilde{f}_T \eta \sigma \tag{19}$$

where $\tilde{f}_T$, the force per bridging chain, can be estimated as

$$\tilde{f}_T = -\frac{d\tilde{F}_T}{dL_T} = -\frac{d}{dL_T}\left(\frac{1}{2}kT\frac{{L_T}^2}{R^2}\right) = -kT\frac{L_T}{R^2} = -\frac{L_T}{L_0}kT\frac{L_0}{R^2} = -\frac{L_T}{L_0}\tilde{f}_0 \quad (20)$$

where $\tilde{F}_T$ is the free energy per bridging chain and $\tilde{f}_0 \equiv kT(L_0/R^2)$ is a reference force. We use the convention that a positive force means that the applied force is compressional, while a negative force means that the applied force is tensile. Using eqs 19 and 20, f_T, the normal force per unit area, is related to the bridging fraction η by

$$f_T = -\frac{L_T}{L_0}\tilde{f}_0\sigma\eta(L) \quad (21)$$

Note that η is determined by $2L$, the surface separation when the bridges are being formed, while the proportionality constant $(L_T/L_0)\tilde{f}_0\sigma$ between f_T and η is determined by $2L_T$, the surface separation when the force measurements are being performed.

The above estimates for f_T and $\tilde{f}_T$ can be confirmed by more accurate calculations. Johner and Joanny[16] and Zhulina and Halperin[17] have derived the exact equations for force as a function of bridging fraction using the MWC model. Numerical solutions of their equations for strongly stretched bridged brushes yield results that agree well with the above estimates.

V. Telechelic Chains in the Crossed Cylinder Configuration

All of the discussion above refers to telechelic chains attached to *flat* surfaces. In actual experiments, however, due to the difficulty in perfectly aligning flat surfaces, a crossed cylinder configuration is often used. This section discusses how to apply the results obtained above to the crossed cylinder configuration, where the bridging fraction η is different in various places because the surface separation $2L$ is different in various places. This variation in η means that the conventional Derjaguin approximation[34] for treating forces cannot be used. As in the previous section, we assume that the force measurements are performed quickly enough that the number of bridges does not change significantly during the measurement.

We first calculate the total number of bridges formed when the crossed cylinders are compressed together. Under no compression, the closest distance between the cylinders is approximately $2L_0$, and a small number of bridges form in the region where the surface separation is approximately $2L_0$. Let us compress the two cylinders together by the distance $2M$ so that the distance of closest approach decreases to $2L_0 - 2M$. By looking at the geometry of the crossed cylinder configuration, we find that the total number of bridges is

$$Q = 2\pi R \int_{L_0-M}^{L_0} dL\ \eta(L)\sigma \quad (22)$$

where R is the radius of curvature of each cylinder. We assume that $R \gg L_0$, in which case the brush attached to the curved surface of the cylinder is well approximated by the brush attached to a flat surface.

Under moderate compression, $\eta(L)$ is given by eq 17. Thus, for $0 \leq M \lesssim L_0/2$,

$$Q \approx 2\pi R M\sigma\left[c_5\left(\frac{L_0 - M/2}{L_0}\right)\left(\frac{R}{L_0}\right)^2 + c_6\left(\frac{M/2}{L_0}\right)\left(\frac{R}{L_0}\right)^{2/3}\right] \quad (23)$$

where c_5 and c_6 are the same constants as in eq 17. For sufficiently large compression such that $M \gg \xi$, the first term in eq 23 becomes negligible, and eq 23 simplifies to

$$Q \approx c_6\pi R\sigma\left(\frac{M^2}{L_0}\right)\left(\frac{R}{L_0}\right)^{2/3} \quad (24)$$

Thus, for $\xi \ll M \lesssim L_0/2$, the number of bridges in the crossed cylinder configuration scales as the square of the compression distance M, while for the comparable case in the parallel plate configuration, the number of bridges scales linearly with the compression distance $L_0 - L$ (cf. eq 18).

The number of bridges Q between the crossed cylinders can be determined experimentally by a procedure similar to that described above for determining the bridging fraction η between flat surfaces—by measuring the normal force when the bridged brush is highly extended. From the geometry of the crossed cylinder configuration, the total normal force is

$$F_T = 2\pi R\int dL_T\, f_T(L_T) = -2\pi R\int dL_T\frac{L_T}{L_0}\tilde{f}_0\sigma\eta(L) \quad (25)$$

where f_T, the normal force per unit area, is given by eq 21. As in eq 21, $2L_T$ is the surface separation when F_T is measured under strong stretching, and $2L$ is the surface separation when the bridges are being formed. While the curvature of the cylinders has a strong effect on $\eta(L)$, as demonstrated above in the equations for Q, the curvature has a much smaller effect on L_T/L_0. When the bridged brush is highly extended, L_T is large, and the variation $2M$ in the surface separation $2L_T$ due to the curvature of the cylinders is small compared to $2L_T$ itself. Thus, to within a relative error of M/L_T, L_T is constant, and eq 25 simplifies to

$$F_T = -2\pi R\frac{L_T}{L_0}\tilde{f}_0\sigma\int_{L_0-M}^{L_0} dL\ \eta(L) = -\frac{L_T}{L_0}\tilde{f}_0 Q \quad (26)$$

We note that the usual Derjaguin approximation,[34] in which the total force between the crossed cylinders is written as $2\pi R\int dL_T\, f_T(L_T) = 2\pi R F$, where F is the free energy per unit area, cannot be used for the bridged brush under extension. The Derjaguin approximation requires that F be the same function everywhere. In the bridged brush, however, F is a different function in various places because the bridging fraction η is different in various places.

Equation 26 together with eq 23 or 24 predicts the experimentally measurable normal force in terms of the parameters L_0, R, σ, R, etc. Some of these parameters can be eliminated by making an additional measurement. The compressional normal force F_C when the crossed cylinders are compressed together such that the distance of closest approach decreases from the equilibrium separation of $2L_0$ to $2L_0 - 2M$ is[9,35]

$$F_C(M) = 2\pi R F = 2\pi R kT\frac{{L_0}^2\sigma}{R^2}\beta(M) = 2\pi R\tilde{f}_0 L_0\sigma\beta(M) \quad (27)$$

where F is the free energy per unit area and

$$\beta(M) = \frac{\pi^2}{12}\left[\frac{1}{2}\left(\frac{L_0 - M}{L_0}\right)^{-1} + \frac{1}{2}\left(\frac{L_0 - M}{L_0}\right)^2 - \frac{1}{10}\left(\frac{L_0 - M}{L_0}\right)^5 - \frac{9}{10}\right] \quad (28)$$

The Derjaguin approximation *is* applicable in this case because F is the same function everywhere. Equation 27 can be rearranged to

$$\tilde{f}_0 = \frac{F_C(M)}{2\pi R L_0 \sigma \beta(M)} \quad (29)$$

Substituting eqs 23 and 29 into eq 26 yields

$$F_T \approx -\frac{F_C(M)}{\beta(M)}\frac{L_T}{L_0}\frac{M}{L_0}\left[c_5\left(\frac{L_0 - M/2}{L_0}\right)\left(\frac{R}{L_0}\right)^2 + c_6\left(\frac{M/2}{L_0}\right)\left(\frac{R}{L_0}\right)^{2/3}\right] \quad (30)$$

which is valid for $0 \le M \lesssim L_0/2$. Restricting M to $\xi \ll M \lesssim L_0/2$, the first term in eq 30 becomes negligible, and eq 30 simplifies to

$$F_T \approx -\frac{F_C(M)}{\beta(M)}\frac{L_T}{L_0}\left(\frac{M}{L_0}\right)^2\left(\frac{R}{L_0}\right)^{2/3} \quad (31)$$

where numerical prefactors have been omitted. By using F_C, eqs 30 and 31 predict the experimentally measurable normal force F_T without referring to σ, the grafting density, or R, the radius of curvature of the cylinders.

The ideas used in calculating normal forces can be readily extended to treat transverse forces that arise under shear. We treat each of the bridging polymers as an ideal spring, as in eq 20, so that a transverse displacement δ produces a transverse restoring force per bridging chain of

$$\tilde{f}_{shear} = \frac{d}{d\delta}\left(\frac{1}{2}kT\frac{\delta^2}{R^2}\right) = kT\frac{\delta}{R^2} = \frac{\delta}{L_0}\tilde{f}_0 \quad (32)$$

Thus, the total transverse restoring force of the Q bridging chains in the crossed cylinder configuration is

$$F_{shear} = \tilde{f}_{shear}Q = \frac{\delta}{L_0}\tilde{f}_0 Q \quad (33)$$

For moderate compression M such that $\xi \ll M \lesssim L_0/2$, the total transverse force is

$$F_{shear} \approx \frac{F_C(M)}{\beta(M)}\frac{\delta}{L_0}\left(\frac{M}{L_0}\right)^2\left(\frac{R}{L_0}\right)^{2/3} \quad (34)$$

Both the transverse force F_{shear} and the normal force F_T can be used to infer the number of bridges Q, and the two measurements could serve as a useful check on each other.

VI. Conclusion

In the theory presented above, we have sketched a quantitative picture of how bridging between surfaces may be induced and how the bridges so produced influence the adhesion between the surfaces. The purpose of our work is to guide future measurements in the surface forces apparatus. Our predictions are based on several idealizations. We have assumed that the sticking and unsticking equilibrium is slow, so that the surfaces may be moved large distances without causing the stickers to detach or slide along the surface. For certain systems, this appears to be a reasonable assumption.[6] In addition, we have assumed strong stretching of the brushes and idealized mean-field behavior of the solvent. These latter assumptions have proven reasonable in predicting real brush properties.[36] Comparing our predictions with experimental measurements should prove instructive.

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