

# Theory of Friction between Neutral Polymer Brushes

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**ABSTRACT:** A type of static friction between two polymer brush coated surfaces resulting from fluctuations from mean-field theory is found, but with creeplike motion for forces below the force of static friction, which is much more rapid than the usual creep between solid surfaces in contact. At sufficiently light loads, it is shown that polymer brush coated surfaces can slide, with the load supported entirely by osmotic pressure, and thus exhibit no static friction and only extremely weak viscous kinetic friction.

## 1. Introduction

A polymer brush consists of a surface with a fairly concentrated coating of polymer chains, each one of which has one, and only one, of its two ends tightly bound to the surface. The mean spacing of the points of attachment to the surface is much smaller than the radius of gyration of an isolated polymer. Aside from the end that is attached to the surface, the remainder of each polymer interacts very weakly with the surface. Polymer brushes serve as extremely effective lubricants, producing friction coefficients as low as 0.001 or less.<sup>1</sup> They must be immersed in a liquid which is a good solvent for the polymers making up the brush in order to function as a lubricant. It will be shown that a reasonably light load can be supported entirely by osmotic pressure due to the solvent, resulting in extremely low viscous friction. Since joints in the human body are known to be immersed in a fluid, known as the synovial fluid, it is possible that they are lubricated by some type of polymer brush consisting of polymers known as lubricin which are attached to the cartilage which coats the bones making up the joints.<sup>2</sup> The density profile of a polymer brush (i.e., the density of monomers as a function of distance from the surface to which the polymers are attached) is well established.<sup>3,4</sup> What is not understood is how the interaction of polymer brush coated surfaces in contact with each other is able to account for the observed friction. For example, molecular dynamics studies generally do not predict static friction,<sup>5</sup> whereas surface force apparatus measurements due to Tadmor et al.<sup>6</sup> report a force of static friction. What is observed is that the shear force between the surfaces of the surface force apparatus increases quite rapidly as a function of degree of sliding, reaches a maximum value, and then decreases as the sliding continues. Presumably, if the force that produces the sliding were below this maximum value, the sliding would cease, although a small amount of motion, due to the elasticity of the polymer brushes and the apparatus, would continue for a short time. This fits the usual definition of static friction. The static friction that they report increases logarithmically with the time that the polymer coated surfaces are in contact (see Figure 1 in ref 6). The logarithmic increase of static friction with resting time is qualitatively similar to a similar effect for solid–solid contact, even though the mechanisms for it are much different.<sup>7</sup>

Pincus, Witten, Milner, etc.,<sup>3,4</sup> present the following picture: over all except the very outer edge of a brush, the monomer

density at a distance  $z$  from the solid surface has the form  $A - Bz^2$ , where  $A$  and  $B$  are constants, but there is a low-density tail for  $z > h_{\max} = (A/B)^{1/2}$ , where  $h_{\max}$  is the height of an uncompressed polymer brush. When two brushes are put in contact they are compressed, and the resulting elastic force (which is really of entropic origin) supports the load.

Kinetic friction is discussed in a paper by Joanny,<sup>8</sup> assuming that it occurs by reptation of polymers from one brush that get entangled in the second brush. He finds only a viscous friction, but if the polymers near the interface get entangled enough, there must be something that resembles static friction if the times scale associated with the reptation motion is very long compared to the time for the surfaces to move some very small distance in creep motion as they attempt to slide. Even for solid–solid friction, there can be creep motion.<sup>9</sup> We shall see, however, that creep for the polymer brushes happens over a much shorter time scale than for bare solid–solid contact.

In this article, it is shown that, as a result of fluctuations from mean-field theory, polymer brushes in contact will exhibit a type of static friction, resulting from interpenetration of polymers belonging to one brush into the second. This is not the usual static friction between solid surfaces in contact, for which when a force below it is applied, the surfaces are stationary for extremely long times. For polymer brush coated surfaces, in contrast, there is relatively rapid creep motion, which can be a few millimeters per hour or faster. The mechanism for friction discussed in this article is to be distinguished from the mechanism for friction discussed in ref 1a. The mechanism in ref 1a is a mechanism for viscous kinetic friction in a region in which the monomer density is in the dilute limit (as might occur in a region between but outside of the main part of the monomer density profile of the two brushes). The friction in this mechanism results from viscous drag as blobs from a polymer are dragged through such a region. It is also shown in the present work that at lighter loads the polymer brushes can support the load without the mean-field theory monomer profiles of the brushes being in actual contact. In this case, the load is entirely supported by osmotic pressure due to the monomers that fluctuate into the interface region between the two brushes. The osmotic pressure in this case is not of the usual textbook example in which a solute is trapped in an impenetrable membrane. Here what plays the role of the membrane are the forces that hold the monomers together in each polymer chain. Since each polymer is anchored to a one of the two surfaces,

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the monomers cannot escape from the region between the two surfaces. Solvent is pulled into the region between the plates to dilute the monomer density, resulting in osmotic pressure.

## 2. Calculation of Friction between Polymer Brushes in Contact

This section deals with a type of static friction expected to occur for two polymer brush coated surfaces in contact. Although the creep rate estimated in the present work is considerably faster than that between typical bare surfaces in contact and under shear stress, it can still be sufficiently slow to allow one to define a force of static friction. In order to calculate the static friction, it is necessary to determine the number of monomers belonging to polymers of one brush that penetrate into the second brush. This can be accomplished using an approach similar to that used in refs 3 and 4. Consider two polymer brushes which are pressed together. The mean-field potential for the hard core interaction of a monomer belonging to a polymer under consideration with other monomers is given by

$$w[\phi(z) + \phi(D - z)] \quad (1)$$

where  $D$  is the separation between the surfaces, to which the two polymer brushes that we are considering are attached,  $z$  is the distance from one of the two surfaces, which we will consider to be the lower surface,  $\phi(z)$  is the monomer density of one of the polymer brushes, and  $w$  is the standard monomer excluded volume parameter.<sup>10</sup> In equilibrium,  $\phi$  has the standard parabolic density<sup>3</sup>

$$\omega\phi(z) = A - Bz^2 \quad (2)$$

for  $z < h$  and zero for  $z > h$ , where  $h$  is the actual height of the brush and  $B = \pi^2 k_B T / (8a^2 N^2)$ , the value that  $B$  must have in order for a polymer attached on one end to the surface at  $z = 0$  to be a solution to the equations of equilibrium, as will be shown explicitly under eq 4. The quantity  $A$  can be written as  $A = Bh_{\max}^2 [(2/3)(h_{\max}/h) + (1/3)(h/h_{\max})^2]$ , which represents the free energy of the brush and is minimum for  $h = h_{\max}$ , which denotes the equilibrium height when the brushes are not in contact with each other. In ref 3, it is shown that  $h_{\max} = (12/\pi^2)^{1/3} (a^2 \sigma w / k_B T)^{1/3} N$ , where the factors of  $k_B T$  and  $a$ , which were set equal to one in ref 3, have been inserted here. Here,  $a$  is the intermonomer distance,  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $\sigma$  is the number of polymers belonging to the polymer brush attached to the surface per unit area.

When the brushes are in contact and the two brushes are pushed together under a load,  $h < h_{\max}$ , which means that the brushes get "flattened out" so that  $\phi(z)$  no longer goes to zero at  $z = h$ . Within mean-field theory, which is expected to be accurate for sufficiently large  $N$ , almost all of the monomers belonging to the brush coating the lower surface remain within that brush, and the monomers belonging to the brush coating the upper surface remain in that brush. For all finite values of  $N$ , however, there exist fluctuations from mean-field theory in which polymers from the lower brush penetrate into the upper brush and polymers belonging to the upper brush penetrate into the lower one. In order to calculate the degree of penetration, let us consider the free energy needed to add a polymer to one of the brushes,<sup>3</sup> which represents the single polymer free energy

$$F(k) - F(k-1) = \int_0^N dn \left[ (1/2)(k_B T/a^2) \left| \frac{d\mathbf{r}_n}{dn} \right|^2 + w(\phi(z_n) + \phi(D - z_n)) \right] \quad (3)$$

where  $F(k)$  is the free energy for a two brush system containing  $k$  polymers and  $r_n$  is the location of the  $n$ th monomer in the polymer that was added to the lower brush.<sup>3</sup> Here,  $z_N$  denotes the  $z$  component of the location of the monomer at the end of the polymer which is attached to the surface and  $z_0$  is the location of the opposite end of the polymer under consideration, which can have any value less than  $h$ . The minimum of the single polymer free energy given in eq 3 is a local equilibrium configuration for the polymer under consideration. We can find a local minimum value of eq 3 by setting the variation of this expression with respect to  $\mathbf{r}_n$  equal to zero, which gives

$$(k_B T/a^2) \frac{d^2 z_n}{dn^2} = w \left[ \frac{d\phi(z_n)}{dz_n} + \frac{d\phi(D - z_n)}{dz_n} \right] \quad (4)$$

which looks like Newton's second law in classical mechanics with the parameter  $n$  playing the role of time and with  $dx_n/dn = dy_n/dn$  are constant. The solutions of eq 4 are subject to the condition that the  $n = N$  monomer lies on the surface to which the polymer under consideration is attached. This means that the solution for  $z_n$  for a polymer attached to the surface at  $z = 0$  satisfies the condition  $z_N = 0$ .

For  $z < h$ , eq 4 is

$$(k_B T/a^2) \frac{d^2 z}{dn^2} = w \frac{d\phi(z)}{dz} = -2Bz \quad (5a)$$

which has the form of Newton's second law for a simple harmonic oscillator. The solution to this equation for  $z_0 < h$ , subject to the condition that  $z_N = 0$ , is

$$z_n = c \cos(\omega n) \quad (5b)$$

where  $c$  is a constant, the choice of "frequency"  $\omega = (2Ba^2/k_B T)^{1/2} = \pi/(2N)$  guarantees that  $z_N = 0$  for all polymers in this brush, and  $c = z_0 < h$ . These are the mean-field theory equilibrium solutions for a polymer belonging to the brush attached to the surface at  $z = 0$ . By a similar argument, the solution for  $z_n$  for a polymer attached to the surface at  $z = D$  is

$$z_n = D + a \cos(\omega n) \quad (5c)$$

with  $\omega$  given above and  $a = -z_0 > -h$ . These are the equilibrium solutions within mean-field theory. In mean-field theory, for any finite value of  $N$ , there is always penetration, resulting from thermal fluctuations, which can be estimated to lowest order in  $1/N$  by solving eq 4 for a polymer which is attached to the surface at  $z = 0$  and penetrates into the region for which  $z > h$ . For  $z_n > h$  for two brushes in contact (i.e., for  $D < 2h_{\max}$ ), eq 4 reduces to

$$(k_B T/a^2) \frac{d^2 z}{dn^2} = w \frac{d\phi(D - z)}{dz} = -2B(z - D) \quad (6a)$$

The solution of eq 6a is

$$z = D + a \cos(\omega n) + b \sin(\omega n) \quad (6b)$$

If we assume that for  $n > k_1$ , the value of  $n$  for the monomer belonging to a polymer connected to the lower surface, which first penetrates into the second brush, we must demand that the

values of  $z_n$  given by eqs 5b and 6b and their derivatives with respect to  $n$  be equal at  $n = k_1$ , since these are second-order differential equations. This condition gives

$$a = -h[\cos(\omega k_1) - \sin(\omega k_1) \tan(\omega k_1)] \quad (7a)$$

$$b = -2h \sin(\omega k_1) \quad (7b)$$

$$c = \frac{h}{\cos(\omega k_1)} \quad (7c)$$

Since we expect for large  $N$  and low temperature that  $k_1 \ll N$ , we find from eq 6b, using eq 7 that

$$z_0 - h \approx (3/2)h(\omega k_1)^2 \quad (8a)$$

and

$$\left. \frac{dz_n}{dn} \right|_{n=0} \approx -2h\omega^2 k_1 \quad (8b)$$

Following the discussion in ref 3, we find that the increase in the free energy of a polymer belonging to the lower brush when  $k_1$  of its monomers penetrate into the upper brush is equal to the amount of work by the tension that would have to be applied to the  $n = 0$  monomer (which is equal to  $(k_B T/a^2)(dz_n/dn|_{n=0})$ ) to pull it out of the lower brush by an amount  $y = z_0 - h$ , which is given by

$$\Delta S = (k_B T/a^2) \int_h^{h+y} \left. \frac{dz_n}{dn} \right|_{n=0} dz_0 \quad (9)$$

If we change variable of integration to  $k_1$  using eq 8, we obtain

$$\Delta S = 2(k_B T/a^2)\omega^4 h^2 k_1^3 \quad (10)$$

Using eq 10, we find that the probability of  $k_1$  monomers of a polymer from the lower brush penetrating into the upper brush is given by the Boltzmann factor

$$e^{-\Delta S/k_B T} = \exp[-2\omega^4 (h/a)^2 k_1^3] \quad (11a)$$

Thus, from eq 11a we conclude that the mean number of monomers of one polymer belonging to one brush that gets entangled in the second brush  $\langle k_1 \rangle$  is of order  $[(1/2)(a/h)^2 \omega^{-4}]^{1/3}$ , which can be written as

$$\langle k_1 \rangle / N = 2/\pi^{4/3} (N^{1/2} a/h_{\max})^{2/3} u^{-2/3} \quad (11b)$$

where  $u = h/h_{\max}$ . The quantity  $N^{1/2}a$  is recognized as the radius of gyration for a nonswollen polymer,<sup>10</sup> which as we see gives a length scale for  $h$ . If  $h$  is comparable to or less than  $N^{1/2}a$ , the fraction of monomers that fluctuate out of the classical mean-field monomer density profile of ref 3 is large, signifying that this mean-field theory must break down at that point. In fact, once  $h < N^{1/2}a$ , it is certainly less than  $N^{3/5}a$ , the Flory radius, signifying that we no longer have a polymer brush. For the case for the experiments reported in ref 6, as  $N \approx 1300$ ,  $h_{\max} = 480$  Å and  $a \approx 5$  Å. From eq 11b one concludes that even for  $h = h_{\max}$ ,  $\langle k_1 \rangle$  is about 22% of  $N$ . One must keep in mind, however, that the theoretical treatment employed here is only expected to give rough orders of magnitude for and scaling relations between the quantities of interest for this problem. In fact, numerical calculations based on mean-field theory<sup>11</sup> and molecular dynamics simulations<sup>5</sup> show that the actual value of the ratio  $\langle k_1 \rangle / N$  is actually noticeably smaller than this value, which



**Figure 1.** Mechanism for friction discussed here is illustrated for just two blobs for clarity. Dark lines represent polymers belonging to a polymer brush. The red lines represent a polymer that has penetrated into the brush represented by the dark lines. The mesh spacing in which these blobs reside are of size  $\xi$ , which is actually a correlation length, rather than a static mesh spacing.<sup>10</sup> Its size is exaggerated here. In reality,  $\xi$  is only a factor 2 larger than the mean intermonomer spacing within an interpenetrating blob.

is not totally unexpected. Nevertheless, it is clear from the present results that for values of  $h$  well below  $N^{1/2}a$  the mean-field treatment of polymer brushes<sup>3,4,10</sup> is not expected to be applicable to this system. Therefore, the discussion in this article will be restricted to sufficiently large values of  $N$  and/or sufficiently dense packing of polymers on the surfaces so that the condition for applicability of mean-field theory,  $\langle k_1 \rangle / N \ll 1$ , is satisfied. Understanding the predictions of mean-field theory, which is a manageable theoretical problem, is a first step toward understanding the mechanisms for friction between polymer brushes. As will be seen, this approach shows tendencies toward the observations reported in ref 6, as the limit of highly compressed brushes studied in that work is approached. A study of the concentration limit needed to obtain a complete understanding of the work of ref 6 will be considered in future work using other approaches.

If the  $\langle k_1 \rangle$  segments belonging to one brush, which penetrate into the second, are sufficiently long to form “blobs” which are close packed in the brush that it has penetrated, one must apply a force to disentangle these blobs, which we identify with the force of friction. This is expected to occur when the polymers belonging to the two brushes are in the semidilute regime.<sup>10</sup> The formation of blobs for a polymer that penetrates a semidilute solution of polymers (as exists for a polymer brush into which it has penetrated) is illustrated in Figure 1. The condition for most parts of the polymer brushes to be in the semidilute regime is  $cR_F^3/N \gg 1$ . Since  $c \approx (N/s^2 h_{\max})$ , this inequality becomes  $(N/s^2 h_{\max})(R_F^3/N) \gg 1$ . We may write  $R_F$  in terms of the interaction parameter  $w$  as  $R_F = (w/k_B T)^{1/5} a^{2/5} N^{3/5} = R_1 N^{3/5}$ , where  $R_1 = (a^2 b^3)^{1/5}$  and where  $b = (w/k_B T)^{1/3}$ . Substituting the expressions for  $R_F$  and  $h_{\max}$  given above, we find that the left-hand side of the last inequality is equal to  $(h_{\max}/s)^{4/5}$ , implying that the brushes will be in the semidilute regime as long as  $h_{\max} \gg s$ . The mean value of the monomer density in the region of the brush into which the polymers from the other brush have penetrated is approximately equal to

$$c = \phi(z = h) = (N/s^2 h_{\max})(\alpha/u) \quad (12)$$

where  $s$  is the distance between polymers at a surface, defined by  $\sigma = s^{-2}$  and  $\alpha = (1 - u^3)$ . Then, from ref 10, the mesh size in the brush is approximately  $\xi = R_F(cR_F^3/N)^{-3/4}$ . (The parameter  $\xi$  actually represents a correlation length, as opposed to the dimension of a static mesh.) Substituting the relationship  $R_F^3/(s^2 h_{\max}) = (h_{\max}/s)^{4/5}$  in the above expression for  $\xi$ , we obtain



$\xi = R_1(Ns/h_{\max})^{3/5}(u/\alpha)^{3/4}$ . The mean number of monomers that get entangled in a brush to which they do not belong  $\langle k_1 \rangle$  can form blobs of size  $\xi$ ,<sup>10</sup> provided that  $\langle k_1 \rangle$  is greater than  $g$ , the number of monomers in a blob of linear size of the order of  $\xi$ . The quantity  $g$  is given by  $g = (\xi/R_1)^{5/3}$ . Substituting the above expression for  $\xi$  in this expression, we obtain

$$g = (Ns/h_{\max})(u/\alpha)^{5/4} \quad (13)$$

If  $\langle k_1 \rangle$  is greater than  $g$ , there is a force of static friction  $f$  per polymer that penetrates, which is the force needed to pull a "blob" through the mesh, (illustrated in Figure 1) which is (from section I.4.1 in ref 10) given by

$$f = \frac{k_B T}{\xi} \quad (14)$$

If  $\langle k_1 \rangle$  is not greater than  $g$ , there will be no static friction. As will be discussed later, this is not true static friction of the usual kind, because even when a force per polymer less than  $f$  is applied, there will be observable motion on time scales considerably shorter than the time scales usually associated with creep motion under applied forces below the force of static friction. From the above condition for the occurrence of static friction, namely  $\langle k_1 \rangle > g$ , we find from eqs 11b and 13 that the relative brush height  $u$  below which there will be static friction satisfies

$$\frac{u^{23/12}}{\alpha^{5/4}} < (2/\pi^{4/3})(N^{1/2}a/h_{\max})^{2/3}(h_{\max}/s) \quad (15)$$

There are two regimes of solutions to eq 15. When the right-hand side of the inequality is greater than one, there will be static friction for all values of  $u$ , below a value which is very close to one (when  $\alpha^{-1}$ , defined under eq 12, is large). The reason for this is that since  $u$  is always less than or equal to 1, the left-hand side of the inequality will be less than one, except for values of  $u$  for which  $u$  is sufficiently close to 1 so that  $\alpha$  is sufficiently small to make the left-hand side greater than one. The cross-over between these two regimes occurs at  $u$  approximately equal to 0.7. That is, there will be static friction for almost all values of  $u$ . When the right-hand side is less than one, there can be values of  $u$  above which static friction disappears (i.e., when eq 15 is not satisfied). From eq 15, we see that the condition that the right-hand side of this inequality be less than one, namely  $(2/\pi^{4/3})(N^{1/2}a/h_{\max})^{2/3} < (s/h_{\max})$ , is very difficult to satisfy, since in general when the condition for the existence of a polymer brush is satisfied, i.e., the radius of gyration of an isolated polymer is less than  $h_{\max}$  and less than the spacing of polymers attached to the surface (i.e.,  $s$ ),  $N^{1/2}a/h_{\max} > s/h_{\max}$ . This implies that for polymer brushes in contact there will virtually always be friction due to entanglement of the polymers. The static friction per polymer is the force needed to dislodge a blob from the mesh, which is given by

$$f = \frac{k_B T}{\xi} = \left( \frac{k_B T}{R_1} \right) (h_{\max}/Ns)^{3/5} \left( \frac{\alpha}{u} \right)^{3/4} \quad (16a)$$

For  $u$  close to 1, but still small enough so that  $\alpha$  is not too much smaller than 1

$$f\sigma = (6.7 \times 10^3 \text{ N/m}^2)(\alpha/u)^{3/4} \quad (16b)$$

using  $a = 5 \text{ \AA}$  and  $b = 2.42 \text{ \AA}$  the value of  $b$  which gives  $h_{\max} = 480 \text{ \AA}$ , the uncompressed height of the polymer brushes of ref 6.

When a force below the maximum force of static friction is applied to the surfaces, we anticipate that the entangled polymer blobs will get pulled out of the brush in which they are entangled in a time of order

$$\Gamma \approx \left[ \frac{\eta_s \xi^3}{k_B T} \right] N_0^3 \quad (17a)$$

where  $N_0 = \langle k_1 \rangle / g$ ,  $\eta_s$  is the viscosity of the solvent, and  $\xi$  is the blob size, from eq VIII.16 in ref 10. Combining eq 17a and our expressions for  $\langle k_1 \rangle$ ,  $\xi$ , and  $g$ , we get

$$\tau = (8/\pi^4)(\eta_s R_1^3/k_B T)(a/s)^{6/5}(Na/h_{\max})^{4/5} N^2 \alpha^{3/2} / u^{7/2} \quad (17b)$$

Using the values for  $a$  and  $b$  given under eq 16 we obtain  $(8/\pi^4)((\eta_s R_1^3/k_B T) = 0.698 \times 10^{-12} \text{ s}$ , at room temperature for  $\eta = 0.01 \text{ P}$ , the viscosity of water. For more viscous solvents,  $\tau$  will be larger than the values quoted here. On the average, an entangled polymer will work itself free in a time  $\tau$ , resulting in the center of masses of the two surfaces sliding a distance  $s/N_e$  relative to each other, where  $N_e$  is the number of entangled polymers. Multiplying this by the rate at which the entangled polymers disentangle by reptation, which is given by  $\tau^{-1}N_e$ , we get a mean creep velocity of  $s/(\tau)$ . Although for  $u$  comparable to 1 this quantity is of the order of a cm/s, since  $\tau \propto h^{-7/2}$ , as the polymer brushes are compressed more and more,  $\tau$  increases rapidly. For sufficiently long chains which are sufficiently compressed, creep motion will more closely resemble that for applied forces below the force of static friction for bare surfaces in contact. This shows a trend toward the static friction observed in ref 6. For example, for the above values for  $a$  and  $b$  and for  $N = 1300$ ,  $s/\tau \approx 10^{-2} \text{ cm/s}$  for  $u = 0.2$ . If  $N = 10\,000$ , it becomes for this value of  $u$ , approximately  $10^{-4} \text{ cm/s}$ , or about a mm/h.

The normal force per polymer that can be supported by two brushes, each with a parabolic monomer distribution is the derivative of the free energy per polymer of one of the brushes given in eq 31 of ref 3, which can be written as

$$F = \frac{N^2 \sigma w}{h_{\max}} \left[ \frac{1}{2u} + \frac{u^2}{2} - \frac{u^5}{10} \right] \quad (18)$$

where  $u = h/h_{\max}$ . The resulting normal force  $f_N$  per unit area, which is equal to minus the derivative of  $F$  with respect to  $h$  multiplied by  $\sigma$ , is given by

$$f_n \sigma = \frac{N^2 \sigma^2 w}{h_{\max}^2} \left[ \frac{1}{2u^2} - u + \frac{u^4}{2} \right] \quad (19a)$$

which can be written as

$$f_n \sigma = (k_B T/a^3)(Na/h_{\max})^2 (b^3 a/s^4) \left[ \frac{1}{2u^2} - u + \frac{u^4}{2} \right] \quad (19b)$$

The quantity  $f_n \sigma$  is zero for  $u = 1$  and increases as  $u$  decreases, increasing as  $u^{-2}$  for sufficiently small  $u$ . Since the force of friction per unit area from eq 16b increases only as  $u^{-3/4}$  as  $u$  decreases, the friction coefficient decreases as  $u^{5/4}$  for small  $u$ . For  $a = 5 \text{ \AA}$ ,  $b = 2.42 \text{ \AA}$ ,  $s = 84 \text{ \AA}$ , and  $N = 1300$ , the quantity multiplying the square bracketed expression is equal to  $8.33 \times 10^3 \text{ N/m}^2$ . From eq 16b we see that the friction coefficient only becomes small when the brushes are fairly strongly compressed (i.e., for small  $u$ ).

The kinetic friction in the slow speed sliding limit (but still much greater than the creep rate) which must be comparable to the static friction can be found from the Tomlinson model,<sup>12</sup> as follows: We may crudely treat an entangled polymer as a spring, one end of which is moving in a potential possessing several minima, taken to represent the potential due to polymers in the brush in which it is entangled. The opposite end of the spring is assumed to move with a sliding velocity  $v$ . Then the total potential of this polymer is given by

$$V = (1/2)\alpha(x - vt)^2 + u(x) \quad (20)$$

where  $\alpha$  is the force constant of the spring,  $u(x)$  is a potential which possesses several minima (which represents the energy needed to pull a polymer out of a brush in which it is entangled), and  $t$  is the time. If  $\alpha < d^2u(x)/dx^2|_{\max}$ , this potential possesses multiple minima.<sup>12</sup> Here  $d^2u(x)/dx^2|_{\max}$  is the maximum force constant of the bottom of the entanglement potential well. Following the treatment of a semidilute solution of polymers in ref 10, the entanglement potential represents the energy that must be expended to pull a “blob” through the mesh created by the other polymers among which the polymer under consideration is entangled. In order to pull the polymer through the mesh, each “blob” must be stretched so that it will become small enough to fit through. It follows that the force constant of the mesh potential must be equal to the force constant for a single “blob”. Since the chain as a whole consists of a bunch of “blobs” connected in series, the effective force constant of the chain must be equal to the force constant of a single “blob” divided by the number of “blobs” of the polymer chain under consideration which are entangled in the other brush. Then the above condition for multistability will be satisfied, if the stretching of the part of the polymer that is still residing in the brush to which it belongs is not inhibited significantly by the surrounding polymers in the brush. As the chain is pulled through the potential a potential minimum containing the end of the chain periodically becomes unstable, allowing the end of the chain to drop into a potential well of lower energy. When this occurs, the resulting drop in potential energy gets converted into kinetic energy, which is assumed to get rapidly dissipated into excitations of the system. Setting the rate at which such energy dissipation occurs equal to the product of the kinetic friction and  $v$ , we determine that there must be nonzero kinetic friction in the low  $v$  limit. Clearly there can only be multistability of the type described above (and hence “stick-slip” motion) if the time it takes to pull a blob out of a region in which it is entangled is small compared to  $\tau$ , where  $\tau$  is defined in eq 17 (i.e.,  $s/v \ll \tau$ ).

### 3. Floating Polymer Brushes

Let us now consider the possibility that at sufficiently light load the bulk of the two polymer brushes might not be in contact, meaning that the load could be entirely supported by osmotic pressure due to those polymers that extend out of each brush into a thin interface region of thickness  $D - 2h$ . (Because of the osmotic pressure in the interface region,  $h$  will be compressed below  $h_{\max}$ , even though the brushes are not in contact.) If this interface region is sufficiently thick so that the polymers from the two brushes do not entangle to any significant degree, there can be negligibly small static friction. Then, the end of the polymer  $z_0$  is located in the interface region. For the part of the polymer in the interface region ( $0 < n < k_1$ ),  $dz_n/dn = -v_1$ , a constant, and hence  $z_n = z_0 - v_1n$ . For  $n > k_1$ ,  $z_n$  is still given by eqs 5b and 7c. Again requiring continuity of  $z_n$  and  $dz_n/dn$  at  $n = k_1$  and assuming that  $\omega k_1 \ll 1$ , we obtain  $v_1 = h\omega k_1$ ,

and hence, the free energy to pull  $k_1$  monomers belonging to a polymer out of a brush  $\Delta S = (k_B T/a^2) \int_0^{k_1} v_1 dz_0 = (2/3)(k_B T/a^2) h^2 \omega^4 k_1^3$ , and hence the probability that  $k_1$  monomers of the chain penetrate into the interface region is given by

$$P = \exp[-(2/3)(h\omega^2/a)^2 k_1^3] \quad (21a)$$

Hence,  $\langle k_1 \rangle/N \approx (3/2)^{1/3} (a/h\omega^2)^{2/3} = (24/\pi^4)^{1/3} (N^{1/2} a/h_{\max})^{2/3} u^{-2/3}$ . As was pointed out in the last section, this estimate for  $\langle k_1 \rangle/N$  is only an order of magnitude estimate, and numerical mean-field theory calculations generally give a smaller value.<sup>11</sup> In order for there to be no significant penetration of polymers belonging to one brush into the second (which might lead to static friction), we require that

$$D - 2h > z_0 - h \approx h\omega^2 \langle k_1 \rangle^2 \quad (21b)$$

In order to estimate  $z_0 - h$ , the amount that a polymer extends out of the mean-field polymer brush density profile, we must first find  $h$  by setting the osmotic pressure equal to the load per unit area that can be supported by a polymer brush. The mean monomer density in the interface region is  $c \approx [\sigma/(D - 2h)] \langle k_1 \rangle$ . The maximum value of the monomer concentration that can occur without significant penetration of polymers belonging to one brush into the second brush is obtained by substituting for  $D - 2h$  using eq 21b, which gives for the maximum possible monomer concentration  $(2/\pi)^2 (N/s^2 h) (N/\langle k_1 \rangle)$ . As this is greater than the monomer density inside a brush, given by eq 12, since  $\langle k_1 \rangle/N < 1$ , we conclude that  $c$  in the interface region can be made as large as we wish if  $D - 2h$  is made sufficiently small. Even though this expression for the maximum possible value of  $c$  in the interface is can be greater than the monomer density inside a brush, such a situation will never occur. The reason for this is that before this happens the brushes will be subject to very high normal force, which will compress them to comparable densities. Of course, at this point the brushes can for all purposes be considered to be in contact.

If  $D - 2h$  is sufficiently large, we can be in the dilute regime, in which the osmotic pressure is given by<sup>10</sup>

$$P_{\text{osm}} = (1/2)(k_B T/a^3) c a^3 / \langle k_1 \rangle \quad (22)$$

The equilibrium value for  $h$  is obtained by setting this expression for the osmotic pressure equal to the load per unit area given by eq 19b and solving the resulting expression for  $h$ . For  $a = 5 \text{ \AA}$ , the quantity  $(1/2)(k_B T/a^3) = 1.6 \times 10^7 \text{ N/m}^2$ . Then for  $ca^3 \approx 0.002$  (a value below which one is likely to be in the dilute regime, defined below), the osmotic pressure can support a load of order  $10^3 \text{ N/m}^2$ . The dilute regime for the monomers that fluctuate out of a polymer brush can be determined by introducing a Flory radius  $R'_F$  for that segment of the polymer which extends into the interface region, in an analogous manner to which it is defined for a whole polymer, namely  $R'_F = R_1 \langle k_1 \rangle^{3/5}$ . The dilute regime is defined by  $c R'_F / \langle k_1 \rangle \ll 1$ . When this condition is satisfied, the two polymer brush coated surfaces will only exhibit viscous friction (i.e., friction that vanishes as the sliding velocity approaches zero). Using the fact that  $c = \langle k_1 \rangle / [(s^2(D - 2h))]$ , this condition becomes  $\langle k_1 \rangle \ll (s^{10/9} / R_1^{5/3}) (D - 2h)^{5/9}$ . Blobs formed from a segment of a polymer that fluctuates into the region between the two mean-field theory parabolic profiles of the two polymer brushes will not get entangled in polymer segments that fluctuate into this region from the other brush (which if it did occur might lead to static friction) if  $g > \langle k_1 \rangle$ . The number of monomers in a single blob  $g$  defined by  $g = (\xi'/R_1)^{5/3}$ , where  $\xi'$ , the mesh size for the

fluctuating monomers from the second brush, is given by  $\xi' = R'_F(cR'_F^3/\langle k_1 \rangle)^{-3/4}$ . Then from the above condition for being in the dilute region, namely  $cR'_F^3/\langle k_1 \rangle \ll 1$ , we find that  $\xi' \gg R'_F$ , which from the above definitions of  $g$  and  $R'_F$  we find that the latter condition implies that  $g \gg \langle k_1 \rangle$ .

As  $D - 2h$  becomes smaller, the interface region will clearly switch into the semidilute regime, resulting in the occurrence of a type of static friction resulting from monomers belonging to one brush getting entangled in monomers belonging to the second brush, likely to be of the same order of magnitude and have a similar creep rate as the static friction found for the assumed case of brushes which touch each other, considered in the last section. This shows a trend toward the behavior found in ref 6; i.e., the friction only becomes large when the brushes are pushed together with a sufficiently large load.

#### 4. Conclusions

We conclude that entanglement of polymers belonging to one polymer brush in a second brush, in which it is in contact, shows a tendency toward the occurrence of the static friction observed in ref 6 for two polymer brushes in contact, as the number of monomers  $N$  decreases from values for which mean-field theory is valid toward the value of  $N$  for the polymer studied in ref 6, although strictly speaking the mean-field theory used here is only marginally applicable for the polymers studied in that work. Although it was estimated that there is a "creep velocity", which is much larger than the creep velocities found for bare solids in contact, it can be sufficiently small so that on short time scales one can consider there to be static friction. Osmotic pressure alone was found to be able to support a load of the order of  $10^3$  Pa while keeping the polymer brushes sufficiently far apart to prevent the entanglement that results in static friction. When the polymers are charged, counterions can provide about  $10^5$  Pa of osmotic pressure.<sup>13</sup>

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