

## Effects of Polydispersity in the End-Grafted Polymer Brush

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**ABSTRACT:** We consider the effects of polydispersity in molecular weight on the equilibrium statistics of the grafted polymer brush. We use a self-consistent field method, exploiting the fact that the chains in the brush are strongly stretched, to map the problem onto one involving the trajectories of classical particles. A general solution for the density or pressure profile and the force required to compress a brush is given in terms of the distribution of molecular weights. The profile is a unique function of the molecular weight distribution and vice versa. Results are also given for a "brush" whose density profile is constrained to be uniform, as is appropriate to the description of lamellar mesophases of block copolymer melts. Consequences for force-balance experiments and for colloid stabilization are discussed.

## I. Introduction

The properties of polymers adsorbed at solid-liquid or liquid-liquid interfaces are important in such diverse areas as tribology, biophysics, and stabilization of colloids. One type of adsorption is "grafting" or end-adsorption, in which polymer chains are attached by one end to a surface. This may be achieved in several ways, including (1) constructing a diblock copolymer in which one block is strongly adsorbed onto the surface,<sup>1</sup> (2) attaching an ionic or zwitterionic group to the end of the polymer chain,<sup>2</sup> or (3) adsorbing a diblock copolymer at the interface between two immiscible solvents, each of which is preferred by one of the polymer blocks.

The resulting structure, called a "brush" because the polymers stretch away from the grafting surface, has been studied previously for the monodisperse case, i.e., when all the chains are of the same molecular weight  $N$ . Energy-balance<sup>3</sup> and blob<sup>4</sup> arguments have been used to show that, as a function of molecular weight and surface coverage  $\sigma$ , the thickness of the brush  $h$  scales as  $N\sigma^{1/3}$  and the free energy per unit area  $F$  scales as  $N\sigma^{5/3}$ .

More recent work<sup>5,6</sup> has shown that these simple scaling arguments miss several important features of the brush, namely, (1) the conformations of different chains in the brush are not necessarily similar, nor is a particular chain uniformly stretched, (2) the density profile, rather than being nearly a step function as was suggested,<sup>3,4</sup> is instead parabolic, and (3) because the density profile goes continuously to zero at the outer extremity of the brush, the force to compress the brush slightly is weaker (by one power of the strain) than calculated by using a step-function ansatz profile.

Of course, polydispersity in molecular weight of polymers is ubiquitous, particularly in commercial-grade samples; thus it is important to explore the effects of polydispersity on the properties of end-grafted polymer brushes. It is even possible that brush properties may be tailored, to some extent, by choosing polydisperse chains. An understanding of these effects requires an extension of the equal-time arguments of ref 6 (outlined below) to a case where many molecular weights and thus "transit times" coexist within a single brush.

Our previous results<sup>6</sup> were obtained by a solution of the one-dimensional self-consistent field (SCF) equations,<sup>7</sup> which give a mean-field description<sup>8</sup> of the system valid

for chains at high coverage interacting through a sufficiently weak two-body repulsion. In practice this description should be valid for chains at moderate concentration in a not-too-good solvent;<sup>9</sup> for brevity this limit is referred to below as the "moderate density" regime. A closely analogous treatment was given earlier by Semenov<sup>10</sup> to describe the statistics of chains in a molten block-copolymer system having a lamellar mesophase geometry. This situation corresponds formally to a polymer brush in which no solvent whatever is present; for brevity we will refer to this as the "melt" regime. In both the moderate density and the melt regimes, the solution of the self-consistent field (SCF) equations makes use of the fact that the chains in a brush are strongly stretched. This strong-stretching assumption allows a "classical limit" to be taken, in which fluctuations of chain conformation about the most probable path between its endpoints can properly be neglected.<sup>6,10</sup> What remains is the many-chain problem of finding the self-consistent set of chain paths (and chain-end positions) in a monomer chemical potential  $V(z)$ . This  $V(z)$  is proportional to the average monomer density  $\Phi(z)$  in the moderate density regime. In a melt,  $V(z)$  is fixed by the requirement that  $\Phi = 1$ . In both cases, this many-chain problem was solved exactly, by employing an "equal-time argument"<sup>6,10</sup>, which we now summarize.

First we assume that the polymer chains are all of equal molecular weight and that their free ends are distributed with nonzero density at all distances from the grafting surface, up to the "brush height"  $h$ , beyond which  $\Phi(z > h) = 0$ . (In ref 6, detailed stability arguments are given to demonstrate that the chain end density is indeed nonzero everywhere in the brush.)

Then the self-consistent chemical potential  $V(z)$  must be such that a chain of molecular weight  $N$  may be in equilibrium—with no force applied to its free end—with that end located anywhere in the brush (at  $z_0$ , say). There is then a precise analogy<sup>8</sup> between the most probable path of the chain between  $z = z_0$  and  $z = 0$  and the trajectory of a certain classical particle. Under this analogy, discussed in detail in ref 6, the arc length of the chain (roughly, the monomer index) corresponds to "time", and the degree of local chain stretching to velocity. The fictitious particles move with equation of motion

$$\frac{d^2z}{dn^2} = -\frac{dU}{dz}(z)$$

where the potential energy  $U(z)$  of the fictitious particle is related to the monomer chemical potential  $V(z)$  by  $U(z)$

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= const -  $V(z)$ . (We define  $U(0) = 0$ , and assign  $V(h) = 0$  for equilibrium brushes.) Since there is no tension at the free end of a chain,  $dz/dn = 0$  there; i.e., the particle starts (at "time" zero, at point  $z_0$ ) from rest.

Then it is evident that for monodisperse chains, the potential  $U(z)$  must be an equal-time potential, i.e., it must give the same "time of flight" (chain length) for a particle starting from rest at any distance away from the grafting surface. That is,  $U(z)$  must be a harmonic-oscillator potential, so that  $V(z) = A - Bz^2$ . The coefficient  $B$  then determines the period of the "oscillator"; one-quarter period is the length  $N$  of the chain. The coefficient  $A$  may be determined, e.g., by (1) insisting on a brush profile that accommodates the required number of monomers per unit area and (2) requiring the monomer chemical potential to be zero at the outer extremity of the brush,  $V(h) = 0$ .

In this paper, we construct a complete extension of our description of the monodisperse brush to the case of arbitrary polydispersity. In section II, we shall construct the self-consistent chemical potential for a brush of arbitrary molecular weight distribution. We find that a derivative of the potential is related to the molecular weight distribution via an invertible linear transformation with a simple kernel. Thus there is a continuous one-to-one correspondence between the potential and the molecular weight distribution. Because the potential  $V(z)$  and the density  $\Phi(z)$  are related through the equation of state, this determines the density profile. Along the way, we shall calculate the free energy required to assemble a polydisperse brush; we find that mixing chains of two different molecular weights releases a large stretching energy, which is especially important when the minority species are the shorter chains. In section III, we compute the force required to compress a brush made of polydisperse chains, in the moderate density case [such that  $\Phi(z) \sim V(z)$ ]. In the conclusion, the variety of effects of polydispersity on profile and compression force are surveyed, and implications for force-balance experiments and colloidal stabilization are discussed.

## II. Polydisperse Equilibrium Brushes

As in our previous work on monodisperse brushes, we consider a brush in which the constituent polymer chains may in general have different conformations, be stretched nonuniformly, and have their free ends located anywhere in the brush.

To begin with, we know that the "equal-time" requirement forces the free ends of chains of different molecular weight to *segregate* in the  $z$  direction: the self-consistent potential  $V(z)$  has a unique time-of-flight (molecular weight) associated with each height  $z$  above the grafting surface. All shorter chains will have their free ends closer to the grafting surface than that of any longer chain. This segregation is a general feature of the "classical" long-chain limit for the polydisperse brush.<sup>11</sup> The problem we shall solve, then, is to find the monomer chemical potential  $V(z)$  and the density of free chain ends  $\epsilon(z)$  such that (1) the potential  $V(z)$  is recovered through the equation of state from the sum of the contributions of each chain to the density and (2) each chain is in mechanical equilibrium in  $V(z)$ .

This section is arranged as follows. In section II.A we will find a decoupling of conditions 1 and 2 above, when the value of the potential is itself used as a coordinate. In section II.B the density of free chain ends in "potential space" is found, by using only condition 1 above, without knowing  $V(z)$  and independent of the molecular weight distribution. These results are used to compute the free energy of the polydisperse brush. A general expression for

the potential  $V(z)$  is recovered in section II.C, from condition 2 above. Finally in section II.D, several particular molecular weight distributions are considered as examples. The behavior of  $V(z)$  near the grafting surface and near the outer extremity of the brush are related to behavior of the molecular weight distribution for small and large molecular weights respectively.

**A. Potential as a Coordinate.** The brush problem as described in the Introduction uses the height  $z$  to specify the classical trajectory  $z(n)$  of a chain. This is a natural choice when the monomer potential  $V(z)$ , and thus the kinematic potential  $U(z)$  of the fictitious particles, is known in advance (as for the monodisperse brush). In the present problem,  $U(z)$  is not known but is one of the quantities to be determined. In this situation a different coordinate is more convenient for specifying the trajectories. In what follows we shall make use of the potential  $U$  itself as the coordinate; thus a chain's trajectory may be specified by the value of  $U$  at the position of each monomer  $n$ . We shall define the zero of  $U$  to be at the grafting surface. The coordinate  $U$  increases monotonically with increasing distance  $z$  from the grafting surface to the outer edge of the brush at  $z = h$ . We denote the corresponding maximum value of  $U$  by  $A \equiv U(h)$ .

This  $U$  representation is convenient because the main quantity required to achieve self-consistency depends only on  $U$ . This quantity is the concentration  $\Phi$ . The contribution  $d\Phi(z; z_0)$  of a chain with free end at  $z_0$  to  $\Phi$  at a point  $z$  is the inverse of its velocity:<sup>6</sup>

$$d\Phi(z; z_0) = v^{-1} = 2^{-1/2}(U(z) - U(z_0))^{-1/2} \quad (1)$$

No mention of the positions  $z$  and  $z_0$  is required; we may just as well use  $U$  and  $U_0 = U(z_0)$  as labels.

Thus, the condition that the density be the sum of contributions from all the chains, written

$$\Phi(z) = \int_{z_0}^h dz' \epsilon(z') d\Phi(z; z') = \int_{U_0}^A dU' \epsilon(U') / [2(U - U')]^{1/2} \quad (2)$$

where  $\epsilon(z)$  is the density of chain free ends, may be written equally well as

$$\Phi(U) = \int_U^A dU' \epsilon(U') / [2(U' - U)]^{1/2} \quad (3)$$

where we have defined a "potential-space end density" by  $\epsilon(U) dU \equiv \epsilon(z) dz$ .

Note that eq 3 makes no mention of either the unknown potential  $U(z)$  or the distribution of molecular weights. Thus, given the equation of state relating  $\Phi$  and the monomer chemical potential  $V$ , eq 3 determines  $\epsilon(U)$ . In section II.B, equations of state for both the moderate density and melt cases are considered, and  $\epsilon(U)$  is evaluated; this information is then used together with the molecular weight distribution to compute the free energy of the polydisperse brush, without knowing  $U(z)$ .

The second condition for a self-consistent description of the equilibrium polydisperse brush is that each chain, in equilibrium in the potential  $V(z)$  with no external forces, traverses the space between its free end and the grafting surface with the appropriate number of monomers. In the language of Newtonian particles, the time of flight for each chain must be as specified by the molecular weight distribution.

Again we write this condition using  $U$  as a coordinate. We denote by  $n(U)$  the time of flight of a chain with free end at  $U$ , and the number of chains per unit area of molecular weight less than  $n$  as  $\sigma(n)$ . If  $\sigma(n)$  is specified and

$\epsilon(U)$  is known,  $n(U)$  is determined by counting chains:

$$\sigma(n(U)) = \int_0^U dU' \epsilon(U') \quad (4)$$

The time of flight  $n(U)$  must be given as well by integrating along the path of the chain with free end at  $U$ , which gives the second condition:

$$n(U) = \int_0^U dU' \frac{dn}{dU}(U') = \int_0^U dU' \frac{dz}{dU}(U') [2(U - U')]^{-1/2} \quad (5)$$

This integral equation must be inverted to give  $dz/dU$  as a linear functional of  $n(U)$ ; then  $z(U)$  is given by integrating  $dz/dU$  and  $U(z)$  is obtained by inverting  $z(U)$ . We may expect that since the relation is linear, a general solution can be constructed by superposition from simple molecular weight distributions. This expectation is borne out in section II.C, where  $dz/dU$  is first constructed for a brush of only two molecular weights and then generalized to arbitrary polydispersity.

**B. Energetics.** As discussed in section II.A, the "constitutive equation" eq 3 by itself determines the end density  $\epsilon(U)$  in potential space independent of molecular weight distribution and without knowing  $U(z)$ , once the equation of state has been chosen. Two representative equations of state are  $\Phi = V$  for the moderate density regime (we work in units such that the excluded-volume parameter  $v$  is unity) and  $\Phi = 1$  for a melt.

For both the moderate-density and melt cases, the left-hand side of eq 3 is homogeneous in  $U$ , as is the kernel of the integral equation. Then simple scaling considerations allow us to invert the equation; we have

$$\epsilon(U) = \begin{cases} \frac{2^{1/2}}{\pi} (A - U)^{-1/2}, & \text{melt} \\ \frac{2^{3/2}}{\pi} (A - U)^{1/2}, & \text{moderate density} \end{cases} \quad (6)$$

Considerable information may be obtained from eq 6 without ever finding  $U(z)$ . For example, we can now use eq 4 to find the value of the potential  $U$  at which the free ends of a given molecular weight are located. In particular, setting  $U = A$ ,  $n(A) = \infty$ ,  $\sigma(\infty) = \sigma$ , we find the potential at the outer edge of the brush:

$$A \equiv U(h) = \begin{cases} (\pi\sigma)^2/8, & \text{melt} \\ \frac{3}{2}(\pi^2/12)^{1/3}\sigma^{2/3}, & \text{moderate density} \end{cases} \quad (7)$$

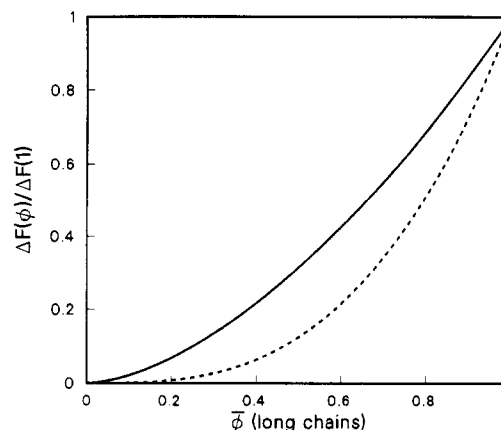
The general relation between  $\sigma(n)$  and  $U(n)$  from eq 4 may be conveniently given in terms of  $A$  as

$$\sigma(n) = \begin{cases} \sigma[1 - (1 - U(n)/A)^{1/2}], & \text{melt} \\ \sigma[1 - (1 - U(n)/A)^{3/2}], & \text{moderate density} \end{cases} \quad (8)$$

Solving for  $U(n)$ , we obtain

$$U(n) = \begin{cases} A[1 - (1 - \sigma(n)/\sigma)^2], & \text{melt} \\ A[1 - (1 - \sigma(n)/\sigma)^{2/3}], & \text{moderate density} \end{cases} \quad (9)$$

In fact, eq 6 gives enough information to compute the free energy of the polydisperse brush. We shall first construct the free energy for a brush made of two molecular weights at total surface coverage  $\sigma$ , with  $\sigma_1$  chains per unit area of molecular weight  $N$  and  $(\sigma - \sigma_1)$  chains per unit area of molecular weight  $M$  ( $M > N$ ). The method is then generalized to arbitrary discrete polydispersity and then the continuum limit is taken.



**Figure 1.** Change in brush free energy,  $\Delta F(\bar{\phi})$ , upon replacing a fraction  $\bar{\phi}$  of the chains of molecular weight  $N$  by chains of molecular weights  $M > N$  shown for both melt- and moderate-density brushes. The y axis scale is the difference between the free energy of a brush made of  $N$  chains and one made of  $M$  chains, i.e.,  $\Delta F(1)$ . The dashed line corresponds to a melt-density ( $\Phi = 1$ ) brush and the solid line to a moderate-density ( $\Phi \sim V$ ) brush.

We make use of some techniques and results of ref 6 to simplify the calculation. The free energy is computed by integrating with respect to coverage  $\sigma$ ; that is, we compute the work to build up the brush chain by chain, adding short and long chains in proportion. We take advantage of the fact that the work required to add a chain of a given molecular weight to the brush is independent of the location of the free end. Thus, focusing on an  $N$  chain with free end very near the grafting surface, the free energy increment to add an  $N$  chain is just  $NV(0) = AN$ .

We recall that the free ends of the chains must be segregated vertically by molecular weight; there is some location  $z_1$  such that  $N$  chain free ends are found for  $0 < z < z_1$ , while  $M$  chain free ends are found for  $z > z_1$ . Now we focus on an  $M$  chain with free end just beyond  $z_1$ . The conformation of this chain is identical with an  $N$  chain with free end just before  $z_1$  but with  $(M - N)$  monomers "dawdling" beyond  $z_1$ . (These extra  $(M - N)$  monomers are analogous to an  $(M - N)$  chain attached to a wall at  $z_1$ ; thus for  $z$  approaching  $z_1$  from above, we must have  $U(z) \sim \text{const} + B_{M-N}(z - z_1)^2$ .) Thus the free energy increment to add an  $M$  chain is just  $AN + (M - N)(A - U(z_1))$ .

We do not yet know  $z_1$ , but we can compute  $U(z_1)$ , by using eq 9 (with  $\sigma(n)$  replaced by  $\sigma_1$ ). Hence the change in free energy of the bimodal brush upon increasing slightly the coverage, with the relative proportion of  $N$  and  $M$  chains fixed at  $\phi \equiv \sigma_1/\sigma$ , is

$$dF/d\sigma = AN\phi + (1 - \phi)(AN + (M - N)(A - U(\sigma_1))) \quad (10)$$

with  $U(\sigma_1)$  given by eq 9. Noticing that  $dF/d\sigma$  is homogeneous in  $\sigma$  ( $\phi$  is fixed,  $A$  and  $U(\sigma_1)$  are given by eq 7 and 9), we may immediately write

$$F = \begin{cases} \frac{1}{3}A\sigma[N + (M - N)(1 - \phi)^3], & \text{melt} \\ \frac{3}{5}A\sigma[N + (M - N)(1 - \phi)^{5/3}], & \text{moderate density} \end{cases} \quad (11)$$

The relative change in free energy of replacing a fraction  $\bar{\phi} \equiv 1 - \phi$  of the  $N$  chains in a brush by  $M$  chains is shown for the melt and moderate density cases in Figure 1. Note the vanishing slope of  $\Delta F(\bar{\phi})/\Delta F(1)$  for small  $\bar{\phi}$ . Because the few lengthened chains are isolated and unstretched, with their extra monomers in a region of vanishingly small density, the work needed to add these tails to the brush is higher order than linear in  $\bar{\phi}$ .

For  $\bar{\phi}$  near unity, the curves of Figure 1 drop more steeply than a linear interpolation between the pure brushes ( $\bar{\phi} = 0$  and  $\bar{\phi} = 1$ ). This is because the scaling result for  $F$  ( $F \sim N\sigma^3$  for a melt,  $F \sim N\sigma^{5/3}$  for moderate density) increases faster than linearly in  $\sigma$ ; since replacing long chains by short ones can be crudely thought of as eliminating them, thus lowering the coverage,  $F$  drops faster than the interpolation.

If we subtract the free energy required to assemble two brushes made of the pure  $M$  and pure  $N$  chains (with the same number  $\sigma$  of chains per unit area), we have the "free energy of mixing" of the  $M$  and  $N$  chains:

$$F_{\text{mix}} = \begin{cases} \frac{1}{3}A\sigma(M-N)[(1-\phi)^3 - (1-\bar{\phi})], & \text{melt} \\ \frac{3}{5}A\sigma(M-N)[(1-\phi)^{5/3} - (1-\bar{\phi})], & \text{moderate density} \end{cases} \quad (12)$$

This free energy of mixing is maximized (at fixed  $\sigma$ ) for a particular value of fractional coverage  $\phi$ , independent of the values of  $M$  and  $N$ ; this value is  $1 - (1/3)^{1/2}$  for the melt case and  $1 - (3/5)^{3/2}$  for the moderate density case.

While we emphasize that we have not solved the problem of a brush composed of two chemically different polymer chains, which would require a different monomer chemical potential  $V(z)$  for each species, we may speculate on the effects on chain compatibility of assembling chains into a brush. The free energy of mixing, eq 12, is proportional to  $M - N$ , while simple estimates of the repulsion between chemically different chains forced to mix in a brush would be proportional to the average of  $M$  and  $N$ . Thus chemically different chains of rather different molecular weight may be compatible in a brush even if they would phase-separate in a bulk solution of comparable concentrations.<sup>12</sup> It may be possible to control phase separation in the plane of the grafting surface of the two species not only by varying temperature (in the usual way) but also by varying the molecular weight difference  $M - N$ .

The same construction used to give the bimodal brush free energy can be used for the case of arbitrary discrete polydispersity, as we now show. Consider a discretely polydisperse brush, i.e., a set of chain molecular weights  $n_1, n_2, \dots, n_i, \dots$  and partial coverages  $\epsilon_1, \epsilon_2, \dots, \epsilon_i, \dots$  ( $\sum \epsilon_i = \sigma$ ); the continuum limit will be taken later. The same argument used to give the free energy increment to add an  $M$  chain to the bimodal brush implies that the free energy  $f_i$  to add a chain of molecular weight  $n_i$  is given by

$$f_i = f_{i-1} + (n_i - n_{i-1})(A - U_{i-1}) \quad (13)$$

with  $f_1 = An_1$  ( $n_0 = U_0 = 0$ ). The continuum limit is clearly  $df(n)/dn = (A - U(n))$ , which may be formally integrated to give  $f(n)$ .

The incremental free energy  $dF/d\sigma$  for increasing the total coverage by one chain per unit area is the average of  $f(n)$ , weighted by the fractional coverage  $\sigma^{-1}d\sigma/dn$  of each molecular weight:

$$\frac{dF}{d\sigma} = \int_0^{\sigma_{\text{max}}} dn' \frac{1}{\sigma} \frac{d\sigma'}{dn'} f(n') = \int_0^{\sigma} \frac{d\sigma'}{\sigma} f(n(\sigma')) \quad (14)$$

Expressing  $f(n)$  as an integral of  $df/dn$ , we obtain a double integral for  $dF/d\sigma$ . This may be simplified by performing the  $n$  integration first:

$$\frac{dF}{d\sigma} = \int_0^{\sigma_{\text{max}}} dn' \int_0^{\sigma(n)} d\sigma' [A - U(\sigma')] \quad (15)$$

Since we know  $U(\sigma)$  explicitly from eq 9, we may express  $dF/d\sigma$  and thence  $F(\sigma)$  itself as an explicit integral of  $\sigma(n)$ :

$$F = \begin{cases} \frac{1}{3}A\sigma \int_0^{\sigma} dn' (1 - \sigma(n')/\sigma)^3, & \text{melt} \\ \frac{3}{5}A\sigma \int_0^{\sigma} dn' (1 - \sigma(n')/\sigma)^{5/3}, & \text{moderate density} \end{cases} \quad (16)$$

**C. Construction of  $U(z)$ .** We now proceed to construct the self-consistent potential  $U(z)$ . Again we use the notation of discrete polydispersity and take a continuum limit at the end. The "time-of-flight" equation, eq 5, is then given by

$$n(U) = \int_0^{U(z)} dU' \frac{dz}{dU'} (U') [2(U - U')]^{-1/2} \quad (17)$$

where  $n(U)$  is piecewise constant, i.e.,  $n(U) = n_i$  for  $U_{i-1} < U(z) < U_i$ . (Here,  $U_i = U(z_i)$  is the value of the potential corresponding to the outer boundary  $z_i$  of the allowed locations of  $n_i$  weight chain free ends and is given by eq 9.  $z_0 = U_0 = 0$ .) This integral equation must be solved for  $dz/dU(U)$ , which may then be integrated to get  $z(U)$ .

As in section II.B, we first consider the case of only two molecular weights  $M$  and  $N$ ; we will then generalize this construction to the polydisperse case. In the monodisperse case, recall that  $U = Bz^2$  and so  $dz/dU = 1/2(BU)^{-1/2}$ ; clearly, this solution works in the polydisperse case for  $z < z_1$ . To construct  $dz/dU$  for the bimodal case, we need only construct  $dz/dU$  for  $z > z_1$ .

From the observation of section II.B that the  $M$  chains whose free ends are located just beyond  $z_1$  "dawdle" near  $z_1$  as if they were  $(M - N)$  chains attached at  $z_1$ , we are led to guess a form for  $dz/dU$  of the two-component brush:

$$\frac{dz}{dU}(U) = \frac{1}{2}[B_{M-N}(U - U_1)]^{-1/2}\Theta(U - U_1) + \frac{1}{2}[B_N U]^{-1/2} \quad (18)$$

which exactly satisfies<sup>13</sup> eq 17 for the bimodal case ( $n_1 \equiv N, n_2 \equiv M$ ). Integrating for  $z(U)$  gives

$$z(U) = \frac{2^{3/2}}{\pi} [NU^{1/2} + (M - N)(U - U_1)^{1/2}\Theta(U - U_1)] \quad (19)$$

where  $U_1$  is given by eq 9 with  $\sigma(n) = \sigma_1$ . This may be inverted to find  $U(z)$  for  $z > z_1$  as

$$U(z) = \frac{B_N}{(1 - \alpha^2)^2} [(1 - \alpha^2)z^2 - 2\alpha z(z^2 - (1 - \alpha^2)z_1^2)^{1/2} - \alpha^2(1 - \alpha^2)z_1^2] \quad (20)$$

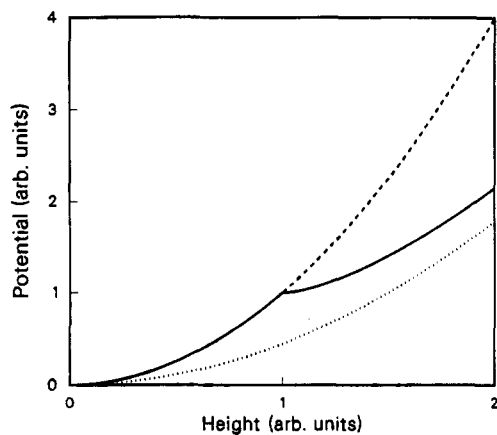
with  $\alpha \equiv M/N - 1$ . (Of course, we have  $U(z) = B_N z^2$  for  $z < z_1$ .) The monomer potential  $V(z)$  vanishes at  $z = h$ ,  $U = U(h) \equiv A$ , so we have  $V(z) = A - U$ . Figure 2 illustrates  $U(z)$  for the molecular weight ratio  $M/N = 2$ .

Since the solution for  $dz/dU(U)$  for a mixture of two molecular weights is the sum of two terms, each term corresponding to one molecular weight, a solution for  $dz/dU(U)$  in the case of general discrete polydispersity can be easily written:

$$\frac{dz}{dU}(U) = \frac{2^{1/2}}{\pi} \sum_i (n_i - n_{i-1})(U - U_{i-1})^{-1/2}\Theta(U - U_i) \quad (n_0 \equiv 0, U_0 \equiv 0) \quad (21)$$

The continuum limit of eq 21 for  $dz/dU$  may be taken, resulting in

$$\frac{dz}{dU}(U) = \frac{2^{1/2}}{\pi} \int_0^{n(U)} dn (U - U(n))^{-1/2} = \frac{2^{1/2}}{\pi} \int_0^U dU' \frac{dn}{dU'} (U') (U - U')^{-1/2} \quad (22)$$



**Figure 2.** Kinematic potential  $U(z)$  shown for a brush composed of a mixture of chains of molecular weights  $N$  and  $M > N$ . The solid curve is  $U(z)$ ; the dashed curves are the potentials for brushes composed of pure  $N$  chains or pure  $M$  chains (here  $M = 2N$ ).

with  $U(n)$  given by eq 9 [which allows the calculation of  $dU/dn(\sigma(U))$ ]. That eq 22 is the solution of the time-of-flight equation, eq 17, can be shown by direct substitution and rearrangement of the integrals.

We may cast eq 22 as a linear functional relation between  $dz/dU$  and the known  $dn/d\sigma$  by using the chain rule and eq 9. This results in

$$\frac{dz}{dU}(U) = \begin{cases} \frac{2^{1/2}}{2\pi A^{1/2}} \int_0^U dU' \frac{dn}{d\sigma}(\sigma(U')) \times \\ (U - U')^{-1/2} (A - U')^{-1/2}, \text{ melt} \\ \frac{3(2^{1/2})\sigma}{2\pi A^{3/2}} \int_0^U dU' \frac{dn}{d\sigma}(\sigma(U')) (U - U')^{-1/2} \times \\ (A - U')^{1/2}, \text{ moderate density} \end{cases} \quad (23)$$

in which  $\sigma(U)$  is given by eq 8, independent of the molecular weight distribution.

Finally, eq 22 may be integrated to find a general expression for the equilibrium height  $h$ :

$$h = \frac{2^{3/2}}{\pi} \int_0^{n_{\max}} dn (A - U(n))^{1/2} \quad (24)$$

**D. Example Molecular Weight Distributions.** We now illustrate this general procedure for the construction of the potential  $U(z)$  (and, hence, in the moderate density regime, also the density profile of the brush), with some specific examples. First consider the uniform distribution with mean  $N$ :

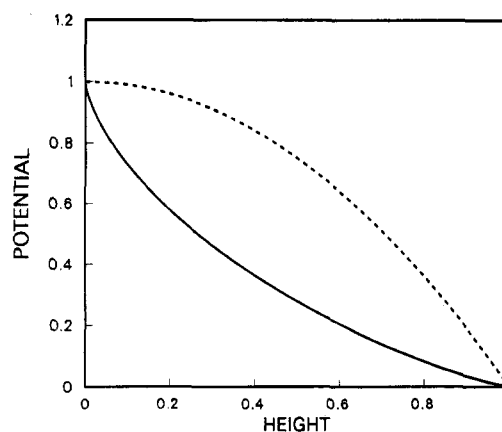
$$\sigma(n) = \frac{\sigma n}{2N} \quad \text{for } n < 2N \quad (25)$$

which by eq 22 quickly yields in the melt case

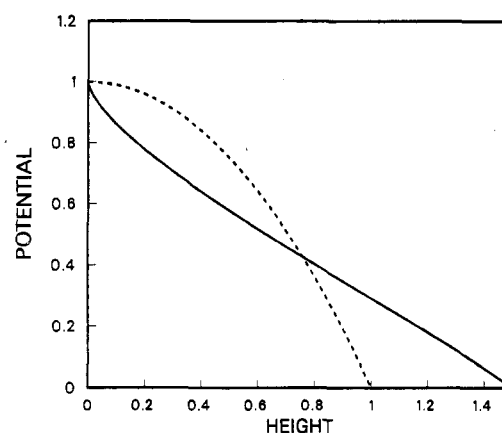
$$\frac{dz}{dU}(U) = \frac{2^{3/2}N}{\pi A^{1/2}} \sinh^{-1} \left( \frac{U}{A - U} \right)^{1/2} \quad (26)$$

For small  $z$ , near the grafting surface, this implies  $U \sim z^{2/3}$ ; at the outer edge of the brush, for  $z$  near  $h$  and  $U$  near  $A$ , we have  $(A - U) \sim -(h - z)/\log(h - z)$ . Numerical integration yields  $U(z)$ , which is compared in Figure 3 to the monodisperse parabola at equivalent mean molecular weight and coverage.

Similar results for the moderate density case with uniform molecular weight distribution (given by eq 25) are shown in Figure 4. The polydisperse brush is here much taller at equilibrium than the monodisperse analogue,



**Figure 3.** Monomer potential  $V(z)$  for a melt-density brush with uniform molecular weight distribution,  $d\sigma/dn(n) = \sigma/(2N)\theta(2N - n)$ , compared to the equivalent monodisperse parabola (same  $N$  and  $\sigma$ ). (The solid curve is the polydisperse brush. The potential is given in units of  $V(0) = A$ , and the height is given in units of the total height of the monodisperse brush.) The cusp for small  $z$  and the logarithmic singularity at  $z = h$  (visible only in the derivative  $dV/dz$ ) are known analytically, as shown in section II.D.



**Figure 4.** Density profile  $\Phi(z)$  of a moderate-density brush with uniform molecular weight distribution (solid curve) compared to that of the equivalent monodisperse brush (dashed curve). (The units are as in Figure 3.) The cusp in  $\Phi(z)$  at small  $z$  and the slope at  $z \sim h$  are obtained analytically in section II.D.

because the longer-than-average chains in the polydisperse case are able to stretch farther from the grafting surface to exploit the relatively low density at the outer fringe of the brush.

Now that we have explicit expressions for the profiles corresponding to some example molecular weight distributions, we consider what new cases may be solved by exploiting the linearity in  $dn/d\sigma$  of eq 23 for the profile. (We have defined the "complementary coverage"  $\bar{\sigma}(n) \equiv \sigma - \sigma(n)$ , which is a convenient quantity for this discussion.) First, let us consider the relationship between this "coverage distribution"  $dn/d\sigma$  and the more familiar molecular weight distribution  $d\sigma/dn$ . We note that the complementary partial coverage  $\bar{\sigma}(n)$  is the number of chains per unit area of molecular weight *greater* than  $n$ . Thus  $\bar{\sigma}(n)$  vanishes at the outer extremity of the brush, where  $n$  is largest. (A larger  $\bar{\sigma}(n)$  corresponds to a smaller  $n$ , so that  $dn/d\bar{\sigma}$  is negative. In the present discussion we may ignore this minus sign.)

For a monodisperse brush with molecular weight  $N$ , the molecular weight distribution  $d\sigma/dn$  is a delta function at  $N$  of strength  $\sigma$ . The corresponding coverage distribution  $dn/d\bar{\sigma}$  is a delta function at  $\sigma$  of strength  $N$ . A smooth, bounded molecular weight distribution yields a

similarly smooth  $dn/d\bar{\sigma}$ . As an example, we consider the uniform distribution of eq 25. Here  $d\sigma/dn$  is a step function nonzero between  $n = 0$  and  $n = N$ . The coverage distribution  $dn/d\bar{\sigma}$  is also a step function, nonzero between 0 and  $\sigma$ .

Since  $F$ ,  $h$ , and  $dz/dV$  are linear functions of  $dn/d\bar{\sigma}$ , one may readily find these quantities for a range of cases not yet considered. Thus, e.g., for a restricted flat distribution with molecular weights between  $N_0$  and  $N$ , the  $dn/d\bar{\sigma}$  is flat for  $\bar{\sigma}$  up to  $\sigma$  with an added delta function at  $\bar{\sigma} = \sigma$  of strength  $N_0$ . This is the sum of the  $dn/d\bar{\sigma}$  distributions for the monodisperse and uniform distributions treated previously. Accordingly, the  $F$ ,  $h$ , and  $dz/dU(U)$  are obtained by adding the results for the simpler cases. We note that these quantities are *not* additive in the molecular weight distribution  $d\sigma/dn$ : e.g., if one combines two populations of chains, each with a known free energy, there is no simple way to infer the free energy of the combined population. (To combine two populations in such a way that their  $dn/d\bar{\sigma}$ 's add, one must add the molecular weights for a given  $\bar{\sigma}$  in each. This amounts to attaching the longest chain in the one population to the longest in the other, the second longest to the second longest, and so forth.)

In general, the computation of the self-consistent potential  $U(z)$  for an arbitrary molecular weight distribution must be performed numerically. However, the asymptotic behavior of this function for small  $z$  (close to the grafting surface) and for  $z \rightarrow h$  (close to the outer extremity of the brush) can be determined directly from the behavior of  $\sigma(n)$  for  $n \sim n_{\min}$  and  $n \sim n_{\max}$ , respectively. To illustrate this, first consider

$$\sigma(n) \sim n^x \quad (27)$$

For the melt case, this leads (for small  $z$ ) to

$$U(z) \sim z^{2x/(2+x)} \quad (28)$$

Note that for  $x = 1$ , corresponding to the uniform distribution above,  $U \sim z^{2/3}$  is recovered, while for  $x \rightarrow \infty$ , corresponding to a monodisperse distribution, the result is  $U \sim z^2$ .

Now consider the effect of a power law in  $\sigma(n)$  near  $n_{\max}$ , i.e.

$$\sigma(n) \sim \sigma - (n_{\max} - n)^x \quad (29)$$

Consider again the case of a melt. If  $0 < x < 1$ , the resulting potential  $U(z)$  has  $dU/dz = \text{const}$  (with logarithmic corrections if  $x = 1$ ) near  $z = h$ . However, if  $x > 1$ , we find

$$A - U \sim (h - z)^{2x/(x+1)} \quad (30)$$

which indicates the range of exponents in  $U(z)$  that can be obtained for distributions with well-defined  $n_{\max}$ .

Similar results are obtained for the moderate-density case, except that for the molecular weight distribution  $\sigma(n) \sim \sigma - (n_{\max} - n)^x$ , we find

$$A - U \sim \begin{cases} h - z, & x < 3 \\ (h - z)^{2x/(x+3)}, & x > 3 \end{cases} \quad (31)$$

Note that the behavior  $dU/dz \sim \text{const}$  near  $z = h$  is "generic" in the sense that a large value of  $x$  is required to violate it. In the limit of large  $x$ , corresponding to a very sparse tail of molecular weight distribution near  $n_{\max}$ , we obtain  $(A - U) \sim (h - z)^2$ .

We now turn to molecular weight distributions with no well-defined maximum molecular weight. For this purpose, we observe that many important properties of the polydisperse brush can be expressed simply as moments of the

"coverage distribution"  $dn/d\bar{\sigma}$  used in eq 23. The free energy  $F$  from eq 16 takes the form

$$F = \begin{cases} \frac{1}{3} A \sigma \int_0^\sigma d\bar{\sigma} (\bar{\sigma}/\sigma)^3 \frac{dn}{d\bar{\sigma}}, & \text{melt} \\ \frac{3}{5} A \sigma \int_0^\sigma d\bar{\sigma} (\bar{\sigma}/\sigma)^{5/3} \frac{dn}{d\bar{\sigma}}, & \text{moderate density} \end{cases} \quad (32)$$

The equilibrium height  $h$  from eq 24 can be expressed as

$$h = \begin{cases} \frac{2^{3/2}}{\pi} A^{1/2} \int_0^\sigma d\bar{\sigma} (\bar{\sigma}/\sigma) \frac{dn}{d\bar{\sigma}}, & \text{melt} \\ \frac{2^{3/2}}{\pi} A^{1/2} \int_0^\sigma d\bar{\sigma} (\bar{\sigma}/\sigma)^{1/3} \frac{dn}{d\bar{\sigma}}, & \text{moderate density} \end{cases} \quad (33)$$

Finally, the inverse of the slope of the potential where it vanishes, given by eq 23 with  $U = A$ , can be written

$$\frac{dz}{dU}(U=A) = \begin{cases} \frac{2^{1/2}}{\pi} A^{-1/2} \int_0^\sigma d\bar{\sigma} (\bar{\sigma}/\sigma)^{-1} \frac{dn}{d\bar{\sigma}}, & \text{melt} \\ \frac{2^{1/2}}{\pi} A^{-1/2} \int_0^\sigma d\bar{\sigma} (\bar{\sigma}/\sigma)^{-1/3} \frac{dn}{d\bar{\sigma}}, & \text{moderate density} \end{cases} \quad (34)$$

The quantities  $F$ ,  $h$ , and  $dz/dU$  are proportional to the  $m$ th moment of  $dn/d\bar{\sigma}$  for various values of  $m$  (with  $m \geq -1$ ). Thus  $F$ ,  $h$ , and  $dz/dU$  are primarily sensitive to the largest values of  $\bar{\sigma}$  and thus to the lowest molecular weights in the distribution. The  $dz/dU$  for the melt is the minus-first moment, and is thus marginal in this respect.

Using eq 32–34, we may discuss broad molecular weight distributions with no maximum molecular weight, a case of some practical importance. We shall consider power-law distributions of the form  $d\sigma/dn \sim n^{-p}$  for large  $n$ . Evidently, we must have  $p > 1$ , or else the total coverage  $\sigma$  is infinite (as are the quantities defined in eq 32–34). This  $d\sigma/dn$  implies a coverage distribution  $dn/d\bar{\sigma} \sim \bar{\sigma}^{-q}$  for small  $\bar{\sigma}$ , where  $q^{-1} + p^{-1} = 1$ .

Such broad distributions may allow a finite  $F$ ,  $h$ , or  $dz/dU$  even with arbitrarily large molecular weights, provided the power  $p$  is large enough. For the moment, we consider the moderate-density case. A finite  $F$  results from eq 32 provided  $p > 5/3$ , so any power which gives a finite coverage  $\sigma$  ( $p > 1$ ) automatically gives a finite free energy. A finite brush height  $h$  requires  $p > 4$ , as one may verify from eq 33. Thus the brush may have a well-defined height for the onset of force even without a well-defined cutoff molecular weight.

For the potential derivative  $dz/dU$ , eq 34 implies that  $dz/dU$  diverges as  $z \rightarrow h$  for any  $p > -2$ , which includes any negative power law in  $d\bar{\sigma}/dn$  extending to infinite  $n$ . Employing eq 23, we find  $V \sim (h - z)^r$ , where  $r = (2p - 2)/(p - 4)$  (and  $p > 4$ , since  $h$  is assumed finite).

When the power  $p$  is near 4,  $V$  increases exceedingly weakly with depth into the brush. But if  $p$  is large, so the molecular weight distribution falls off rapidly,  $V(h - z)$  approaches a quadratic behavior. (This is similar to the behavior obtained with a molecular weight distribution that falls rapidly to zero at a finite  $n_{\max}$ , as eq 29 and 30 with  $x \rightarrow \infty$ .)

The power-law distributions considered above for the moderate density case are also of interest in the melt case. Here the moments are larger in magnitude than their moderate-density counterparts. For  $F$  and  $h$ , a power-law tail has correspondingly less effect. The condition for a finite height is the trivial one that the mean molecular weight be finite:  $p > 2$ . Again, the onset of the potential  $V$  near the brush tip is sensitive to the power  $p$ . For the melt,  $V \sim (h - z)^r$ , where  $r = (2p - 2)/(p - 2)$ . Again the

power  $r$  diverges as the threshold value  $p = 2$  is approached. And again, the limit of a steep power law ( $p \rightarrow \infty$ ) gives rise to a quadratic increase of  $V$ .

### III. Compressed Polydisperse Brushes

Previous work<sup>6</sup> showed that the repulsive force between two brushes brought into contact is equal, within the "classical limit" picture, to the force required to compress a brush with an impenetrable plate. (The equivalence of these two situations is a result of the absence of interdigitation of the brushes in the classical limit.<sup>6</sup>) As the repulsive force between two colloidal particles with end-grafted polymers attached to their surfaces may in some cases be modeled by the repulsion of planar brushes, it is of interest to know the effects of polydispersity on the force needed to compress a brush. (In this section we are of course concerned only with the moderate density regime, since in the melt case the brush is, by construction, incompressible at fixed coverage.)

The expression for the density of chain free ends (eq 6) is modified when the brush is compressed. Equation 3 still holds, and the density  $\Phi(z)$  is still related to the monomer chemical potential  $V(z)$  by  $\Phi(z) \sim V(z)$ . However,  $V(z)$  and the fictitious classical particle potential  $U(z)$  are offset by an additional constant, which is the density  $\Phi(h)$  at the outer edge of the brush. The externally applied pressure  $p$ , which compresses the brush to a height  $h(p)$ , is simply equal to the osmotic pressure at the edge of the brush,  $p = \frac{1}{2}\Phi^2(h)$ . Thus we have  $V(z) = (2p)^{1/2} + U(h(p)) - U(z)$ .

Because the relation between  $\Phi$  and  $U$  has changed, we must recompute the end density for nonzero  $p$ ,  $\epsilon(U;p)$ , from eq 3. This gives [writing  $A(p) \equiv U(h(p))$ ]

$$\epsilon(U;p) = \frac{2^{3/2}}{\pi}(A(p) - U)^{1/2} + \frac{2}{\pi}p^{1/2}(A(p) - U)^{-1/2} \quad (35)$$

Again, eq 9 determines the potential  $U(n)$  at the boundary of the region where free ends of  $n$ -weight chains are found; we now write this as  $U(n;p)$  to make the  $p$  dependence explicit. Integrating eq 4 gives

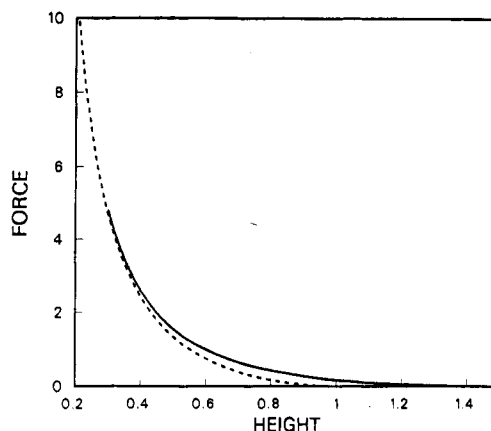
$$\sigma - \sigma(n) = \frac{2^{5/2}}{3\pi} \left[ (A(p) - U(n;p))^{3/2} + \frac{3p^{1/2}}{2^{1/2}} (A(p) - U(n;p))^{1/2} \right] \quad (36)$$

which is a cubic equation for  $(A(p) - U(n;p))^{1/2}$ . (Setting  $n = 0$  and noting  $\sigma(0) = U(0;p) = 0$  give an equation for  $A(p)$ .) The height of the brush under a given compression  $h(p)$  can now be expressed as

$$h(p) = \int_0^{A(p)} dU \frac{dz}{dU}(U) = \frac{2^{3/2}}{\pi} \int_0^{n_{\max}} dn (A(p) - U(n;p))^{1/2} \quad (37)$$

Thus finding  $h(p)$ , the brush compression under external pressure, is reduced for arbitrary molecular weight distribution  $\sigma(n)$  to solving the cubic equation for  $(A(p) - U(n;p))$ , eq 36, and integrating (numerically) eq 37.

As an example, we consider again a brush with a uniform molecular weight distribution as in eq 25; Figure 5 illustrates the features of the force-compression relation for the brush of uniform molecular weight distribution, contrasted with the equivalent monodisperse brush. In section II.D it was found that the equilibrium profile of such a brush (in the moderate density regime) is much more extended, with a much smaller slope near  $z = h$ , than that of the analogous monodisperse system (as shown in Figure 4).



**Figure 5.** Pressure  $p(h)$  required to compress a moderate-density brush with uniform molecular weight distribution to a height  $h$  (solid curve) compared with that of the equivalent monodisperse moderate-density brush (dashed curve). (The force is given in units of the osmotic pressure at the grafting surface in the uncompressed monodisperse brush.) The two curves are identical at large compression and given by the "equation of state"  $p = \frac{1}{2}\Phi^2 = \frac{1}{2}(N\sigma/h)^2$  for unstretched polymers; for small compressions, the curves reflect the uncompressed density profiles near the outer extremity of the brush (see Figure 4).

At large compressions, of course, the two brushes are indistinguishable, since the force is given in this limit by  $p = \Phi^2/2$ , with  $\Phi = N\sigma/h$  being the uniform density of the compressed brush. Hence the two curves in Figure 5 become identical when the brush height  $h(p)$  is much less than the uncompressed height  $h(0)$ .

For small compressions, we may estimate the force from the uncompressed profile by  $p(h) = \frac{1}{2}\Phi^2(h(0) - \delta h)$ . This estimate is valid<sup>6</sup> because the matter displaced by compression is distributed over the remaining brush height in a nonsingular way. Thus for small compressions, the equilibrium profile truncated at some height  $h(p)$  less than the equilibrium height  $h(0)$  is a good approximation to the compressed profile. Hence the force for small compressions is given directly by the density profile near the outer extremity of the brush. Both the force and the profile of the polydisperse brush with  $\sigma$  given by eq 25 vanish at a larger  $h$  and have a smaller slope than the equivalent monodisperse brush (compare Figures 4 and 5). More generally, if the molecular weight distribution has a power-law onset given by eq 29, the force for small compressions is

$$p \sim \begin{cases} (h-z)^2, & x < 3 \\ (h-z)^{4x/(x+3)}, & x > 3 \end{cases} \quad (38)$$

Similar estimates of the force law for compression of the moderate-density brush may be made for the power-law molecular weight distributions considered in section II.D. There, we found that a rapidly decaying molecular weight distribution,  $d\sigma/dn \sim n^{-p}$  with  $p$  large, led to a quadratic dependence of  $V(z) \sim (h-z)^2$  for  $z$  near  $h$ . This quadratic dependence of  $V$ , and hence  $\Phi$ , implies a quartic law for the force ( $\sim \Phi^2$ ) as a function of small compression. By "small" we mean a compression small enough that only long chains described by the power-law tail would normally extend beyond the compressed height.<sup>14</sup>

We expect such a force law not only for power-law molecular weight distributions but also for the more rapid exponential falloff often encountered in practice. One readily verifies that a "most-probable" chain-length distribution, with  $d\sigma/dn \propto \exp(-\gamma n)$ , has a power-law  $dn/d\sigma = (\gamma\sigma)^{-1}$ , so that our previous analysis applies (with  $p \rightarrow$



$\infty$ ) even for finite compressions. Such a chain-length distribution should give a quartic force law up to compressions of order  $h$ .

#### IV. Conclusions

We have extended the "classical limit" method, which consists of approximating the configurations of strongly stretched polymers in a self-consistent field by their most probable configurations (with given free end positions), so as to treat the important case of a grafted polymer brush of arbitrary polydispersity.

In principle our theory predicts (as functionals of the molecular weight distribution) the equilibrium density profile, distribution of chain ends, self-consistent monomer potential, and force-distance relation for a brush in the "moderate density" regime. (Recall that in this regime the monomer potential  $V$  is proportional to the local density of segments  $\Phi$ .) For the "melt regime", in which the segment density  $\Phi$  is constrained to be constant, we have also given expressions for the self-consistent potential and the chain-end distribution. These results generalize the corresponding results for the monodisperse brush that were given (for the melt) by Semenov in ref 10 and (for the moderate density regime) by ourselves in ref 6.

That practical calculations are possible by using this method was shown by treating in detail the cases of a bimodal and a uniform molecular weight distribution. In each case, novel features appeared beyond those discovered previously for the monodisperse brush. One remarkable new prediction is that of the complete stratification, according to molecular weight, of the locations of the free chain ends above the grafting surface. Although for finite chain lengths there is some "smearing" of the stratification due to fluctuations about the classical trajectories, an effect of this kind should nonetheless be observable by careful experimentation. For example, with a bimodal distribution of chain lengths, fluorescent markers attached to the longer chains and quenched by contact with the grafting surface would be extinguished much less frequently than in a monodisperse brush of the same mean molecular weight and number of chains per unit area.

Another new result (section II.B) concerns the free energy of "mixing" two chains of different molecular weights in a brush geometry. We find a term, extensive in the difference in molecular weights, that favors the mixing of chains of different lengths so as to increase the configurational entropy of the brush. This may shift the occurrences of demixing transitions, etc., of chemically different species in a brush from their locations in an unstretched, bulk system of equivalent mean concentration.

The profile and the force required to compress a polydisperse brush can be calculated for arbitrary molecular weight distribution with modest numerical efforts (numerical integration). The features of the profile for small  $z$  and  $z$  near  $h$  can be obtained in terms of the behavior of the molecular weight distribution,  $d\sigma/dn(n)$ , for  $n \sim n_{\min}$  and  $n \sim n_{\max}$ , respectively. The profile is softened at its outer extremity by the addition of some longer chains and made steeper near the grafting surface by the addition of shorter chains.

The force for small compressions, which in applications to colloid stabilization is perhaps the most important regime, is directly related to the uncompressed profile near the outer extremity. For modest power-law onset in  $\sigma(n)$  near  $n_{\max}$  (eq 29), the profile has a finite slope at  $z = h$ , leading to  $p = ch^2$  (eq 38); however, the value of this slope, which fixes the coefficient  $c$  above, depends on the largest molecular weights present in the brush. In some cases the force for small compressions is qualitatively changed by

polydispersity, growing more slowly with compression than the quadratic dependence predicted for the monodisperse brush. For example, with an exponential tail in the molecular weight distribution, the force increases as the *fourth* power of compression. Efforts are under way to model current force-balance experiments on moderately polydisperse samples,<sup>1</sup> in which small-compression measurements appear to differ significantly from predictions for a monodisperse brush. In addition, force-balance experiments on deliberately polydisperse samples (such as the most probable chain-length distribution) would be interesting.

In the "classical limit" analysis, the force of compression vanishes beyond the height  $h$ . But in a real brush, where the chains are not stretched arbitrarily more than their equilibrium size, there are weak forces beyond the height  $h$ . Chains in this region should behave like a *dilute* grafted layer. The detailed properties of this region are important to work out.

The free energy  $F$  and height  $h$  of a brush both give information about its polydispersity. Both  $F$  and  $h$  measure moments of the "coverage distribution"  $dn/d\sigma$ . When the force varies quadratically with compression, the quadratic coefficient also measures a moment of  $dn/d\sigma$ . But when the force varies quartically with compression, the quartic coefficient depends only on the scale molecular weight  $\gamma^{-1}$  (below eq 38).

The results reported here can give the energy required for bending a brush as well as compressing it. We report elsewhere<sup>15</sup> our results for the bending moduli of the polydisperse brush and compare this with recent calculations on surfactant bilayers.

We have given little attention here to experimental consequences of polydispersity in the melt case. Here at fixed coverage the brush is incompressible, so that the force of compression explored above has no exact counterpart. But often in the melt case the coverage is not fixed. For systems such as copolymer lamellae, the coverage arises from a balance of stretching and interfacial energy between the incompatible blocks. We expect the free energy of mixing and the equilibrium lamellar spacing for this case to show interesting dependence on the molecular weight distribution.

**Acknowledgment.** We thank Shlomo Alexander, Pierre-Gilles de Gennes, Jacob Klein, Fyl Pincus, and Matthew Tirrell for helpful conversations. This research was supported in part by NSF Grant No. PHY82-17853, supplemented by funds from NASA at the University of California in Santa Barbara.

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- (10) Semenov, A. N. *Sov. Phys. JETP* 1985, 61, 733 (*Zh. Eksp. Teor. Fiz.* 1985, 88, 1242).
- (11) Of course, fluctuations will smear the "time zone" boundaries over a distance of order  $R_g \sim N^{1/2}$ , which is the characteristic scale of fluctuation corrections to the classical limit. Nonetheless, in the limit of large molecular weight at fixed coverage, the time zones are sharply defined, insofar as  $R_g$  is small compared to the brush height.
- (12) Several situations may be envisioned, depending on the mobility of the chain attachment points along the grafting surface. If the chain attachment points are free to move, we expect complete in-plane phase separation of sufficiently incompatible chains in a brush. If the chain ends are irreversibly attached to the surface, some sort of microphase separation may take place, with a length scale related to the brush height. These phase separations are not to be confused with the segregation by molecular weight of the free-chain ends in the direction *normal* to the grafting surface, which is a quite general phenomenon, as discussed above.
- (13)  $dz/dU \sim u^{-1/2}$  in eq 17 gives  $n = \text{const}$ , which may be anticipated because the integral is then a homogeneous function of  $U$ . Similarly, we may guess that shifting the square root singularity with  $dz/dU \sim (U - U_1)^{-1/2} \Theta(U - U_1)$  may produce  $n(U) = \text{const} \times \Theta(U - U_1)$ , which is exactly what happens.
- (14) There is always a regime of very small compressions, for which the few long chains affected are too dilute to be stretched. Here our classical limit breaks down, and the energies and densities resemble those of *dilute* grafted chains.
- (15) Milner, S. T.; Witten, T. A., to be submitted for publication.

## Chemical Composition Distribution of a Graft Copolymer Prepared from Macromonomer: Fractionation in Demixing Solvents<sup>†</sup>

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**ABSTRACT:** A graft copolymer prepared by radical copolymerization of poly(dimethylsiloxane) macromonomer with methyl methacrylate has been characterized by light scattering and osmometry. The number- and weight-average molecular weights of the whole copolymer, its backbone, and the graft part were determined. Copolymer macromolecules contain five grafts on an average. The copolymer was fractionated in a demixing solvent pair dimethyl sulfoxide-tetrachloroethylene. Fractions differing up to 24 wt % in methyl methacrylate unit content were obtained. The advantages of this novel method of fractionation are discussed. The integral distribution of chemical composition evaluated from the fractionation data agrees well with the theoretical prediction.

### Introduction

Synthesis of graft copolymers by statistical copolymerization of ordinary low molecular weight monomers with macromonomers has recently become an attractive field of research.<sup>1</sup> So far, not much attention has been paid to the characterization of chemical heterogeneity of these copolymers, even though the model calculations predict,<sup>2,3</sup> similarly to block copolymers,<sup>4,5</sup> relatively broad chemical composition distributions (CCD). One of the reasons may be the limited efficiency of the present fractionation methods. Especially in the classical precipitation fractionation, the formation of polymolecular micelles<sup>6</sup> may create serious problems.<sup>7</sup> It should be realized that, in addition to distribution of molecular weights, CCD also may affect the properties of copolymers.

It is the aim of this study to contribute to the methodology of graft copolymer characterization and to confront the theoretically predicted CCD with experimental results. Poly(methyl methacrylate) (PMMA) grafted with poly(dimethylsiloxane) (PDMS), PMMA-*g*-PDMS,<sup>8,9</sup> was selected for this purpose. A separation method based on the distribution of a copolymer between the phases of de-

mixing solvents<sup>10-12</sup> was used to fractionate the graft copolymer according to chemical composition.

### Experimental Section

**Graft Copolymer.** The poly(dimethylsiloxane) macromonomer was prepared<sup>8</sup> by anionic polymerization of hexamethylcyclotrisiloxane (Petrarch Inc.) in cyclohexane with *n*-butyllithium as initiator and tetrahydrofuran as promoter. Termination of living anions with (3-(methacryloxy)propyl)dimethylchlorosilane (Petrarch Inc.) resulted in formation of a macromonomer, which was then precipitated into methanol and dried in vacuo. The number-average molecular weight, determined by vapor-pressure osmometry, was  $M_{nB}^* = 10\,000$ .

Free radical copolymerization of macromonomer with methyl methacrylate (MMA)<sup>8,9</sup> was carried out at 60 °C in toluene with azobisisobutyronitrile as initiator. The isolated PMMA-*g*-PDMS copolymer was extracted with *n*-hexane to remove the residual macromonomer and then dried in vacuo. The average content of PMMA found by NMR was 59.7 wt %.

**Solvents.** Methyl ethyl ketone, tetralin (both from Fluka AG, Switzerland), toluene, dioxane, dimethyl sulfoxide (DMSO), tetrachloroethylene (TCE), and methanol (Lachema, Czechoslovakia) applied in the characterization and/or treatment of the graft copolymer were used as supplied by the manufacturer; only TCE was distilled on a laboratory column.

**Differential Refractometry.** Refractive index increments of PMMA and PDMS ( $M_w = 7000$ ) were determined with a Brice-Phoenix BP-2000-V differential refractometer at 25 °C for a wavelength of 546 nm. The refractive index increments,  $dn/dc$ ,

<sup>†</sup> We are happy to dedicate this paper to Professor O. Wichterle, the founder of Czechoslovak polymer science, on the occasion of his 75th birthday.