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# Chain Behavior in a Polydisperse Brush: Depression of Critical Fluctuations

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**ABSTRACT:** Anomalous end-to-end distance fluctuations  $\langle \delta h^2 \rangle \sim N^2$  characteristic of a monodisperse brush are strongly depressed even in the case of relatively narrow continuous chain length distribution. The magnitude of fluctuation for a typical chain decreases with increasing inhomogeneity parameter  $q = N_w/N_n - 1$  according to a power law  $\langle \delta h^2 \rangle \sim q^{-1/2}$ , implying an analogy between  $q$  and the deviation from the critical point. A  $q$ - $N$  diagram showing different regimes of asymptotic behavior is constructed.

## Introduction

Polymer brushes formed by long enough chains attached by one end to a surface or a liquid-liquid interface have been attracting lately a significant amount of interest (see ref 1 and references cited therein). These studies give valuable insights toward understanding several systems of great practical importance, such as stabilized colloids, block copolymers under microphase segregation, and polymeric compatibilizers. A rather good understanding of different aspects of equilibrium behavior of these systems has been achieved through both experimental and theoretical studies.

Most theoretical approaches in this field are based on a monodisperse system, though some investigations of polydispersity effects have been also carried out.<sup>2-4</sup> Polydispersity is inherent to all synthetic polymers and affects physical and technological properties of the material. In most cases this influence is not at all dramatic and does not display any threshold effects. It becomes significant only for samples differing greatly in degree of polydispersity (which is usually characterized by the ratio  $M_w/M_n$ ). In the case of polymer brushes, this is true for such characteristics as the average thickness and the segment density profile.<sup>2-4</sup> The total effect becomes negligible as long as  $M_w/M_n$  is close enough to 1.

In a previous paper<sup>5</sup> we argued that large-scale chain fluctuations in a monodisperse brush grafted onto a planar surface are of critical nature and correspond to the middle of the coil-stretch transition. This leads also to the anomalously slow large-scale chain relaxation with characteristic time  $\tau \sim N^3$  even in the absence of strong entanglement effects. It was also shown that an "admixture" chain differing in its length from the main chains of the brush might have strikingly different conformation and magnitude of the end-to-end distance fluctuations depending on whether it is shorter or longer than a main chain, provided the fraction of admixture chains in a monodisperse brush is small. This suggests that polydispersity may play an unusually dramatic role with respect to the fluctuational and dynamic behavior of polymer brushes.

One might note also that analytical theory of polydisperse brushes, developed by Milner, Witten, and Cates,<sup>2</sup> if taken quite literally, gives a somewhat paradoxical

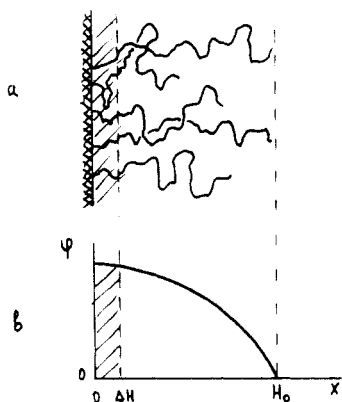
prediction: while in a monodisperse system the free end of a chain fluctuates over the thickness of the entire brush, which is proportional to the contour length of a chain; for any polydisperse brush with a smooth molecular weight distribution, positions of all chain ends appear to be fixed. Of course, this result stems from the Newtonian trajectory approximation the theory is based on. What it really means is that the end-to-end distance fluctuations should be small on the scale of the brush thickness. A question naturally arises: how does the change in the fluctuation behavior take place with the increase in polydispersity of the chains comprising the brush?

That is what the present paper aims to investigate. We derive a specific type of a continuous molecular mass distribution (MMD) which allows analytical treatment of the chain fluctuations. We then show that even a very small polydispersity may lead to depression of anomalous fluctuations and regaining of normal Rouse-type relaxation in a manner similar to critical phenomena. Finally, we construct a diagram for polydisperse polymer chains grafted onto a planar surface showing different asymptotic regimes of chain behavior and compare analytical results with numerical calculations for the same model.

## Model Molecular Mass Distribution

The existing SCF theory of polydisperse polymer brushes<sup>2</sup> allows one to calculate the segment density and effective potential profiles for an arbitrary form of MMD. However, obtaining closed-form analytical expressions for the self-consistent potential in the case of commonly used continuous distributions is very difficult. To have an opportunity of studying a system with both MMD and the potential given by simple analytical formulas, we use the following trick introduced by Zhulina and Borisov.<sup>6</sup> We start from a monodisperse brush formed by flexible chains with the degree of polymerization  $N_0 \gg 1$  and grafting density  $\rho_0$  large enough to ensure chain overlapping  $1 \gg \rho_0 \gg N^{-6/5}$  (the size of the chain segment  $a$  is taken as a unit length). For the sake of simplicity we shall use formulas corresponding to the case of a good solvent, but the qualitative results appear to be of a general nature. Then we "freeze" a slab between the grafting plane and a "ghost" plane displaced by a distance  $\Delta H$  (see Figure 1). The portions of chains that are confined inside the slab are forbidden to fluctuate, and since chains of the original brush had a wide distribution of the degree of stretching, these portions are of different length. From now on we

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**Figure 1.** Polydisperse polymer brush as prepared from a monodisperse one (a) and its segment density profile (b).

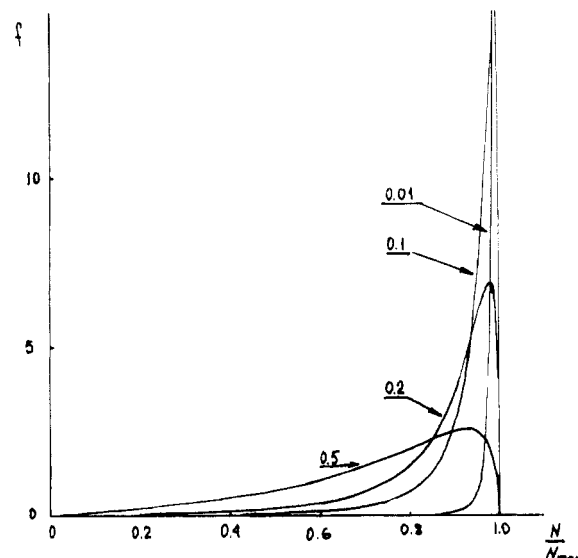
shall consider the ghost plane as a new grafting plane with polydisperse chains attached to it. The structure of the new brush will coincide with that of the outer part of the old one. It should not change in the course of the operation since the original brush corresponded to the minimum of the free energy and freezing some part of the structure does not affect this. Strictly speaking, changing a ghost plane into an impenetrable one is legitimate only if one can neglect the probability of the free portion of a chain to go backward, under the ghost plane. These conformations were possible in the original monodisperse brush, but they are forbidden once the new grafting plane becomes impenetrable. The validity of the trick described above is thus linked to the Newtonian trajectory approximation which neglects the contribution of conformations containing backsteps. This approximation is the basis for analytical theories of polymer brushes<sup>7-9</sup> and, when compared to a more rigorous numerical approach, was shown to work very well<sup>1,10</sup> in the limit of strong stretching ( $H \gg N^{3/5}$ ).

To obtain the molecular weight (or, rather, chain length) distribution for the new brush, we use expressions<sup>8,9</sup> for the distribution of free ends in the original brush,  $g(x') = 3(x'/H_0^2)(1 - (x'^2/H_0^2))$ , and for the local stretching of a chain  $E(x, x') = dx/dn = (\pi/2N)(x'^2 - x^2)^{1/2}$ , where  $x$  is the distance from the grafting plane to the  $n$ th segment,  $x'$  is that for the end segment, and  $H_0$  is the original brush thickness. Only chains with  $x' > \Delta H$  contribute to the formation of the polydisperse brush, which means that its effective grafting density,  $\rho$ , is smaller than that of the original brush:  $\rho = \rho_0 \int_{\Delta H}^{H_0} g(x') dx'$ . The fraction of chains with end height  $x'$  is  $\rho/\rho_0 g(x') dx'$ , and the corresponding chain length is  $N(x') = \int_{\Delta H}^{x'} (dx/E(x, x'))$ . This finally gives the form of the chain length distribution

$$f(N) = \frac{3\pi\alpha^2 \left( \sin^2 \frac{\pi(N_0 - N)}{2N_0} - \alpha^2 \right)^{1/2} \cos \frac{\pi(N_0 - N)}{2N_0}}{2(1 - \alpha^2)^{3/2} N_0 \sin^4 \frac{\pi(N_0 - N)}{2N_0}} \quad (1)$$

where  $\alpha = \Delta H/H_0$ .

This particular type of MMD is asymmetric and is characterized by the finite cutoff chain length  $N_{\max} = N_0(1 - 2/\pi \arcsin \alpha)$  (Figure 2). The greater was the relative displacement of the grafting plane  $\alpha$  the broader is MMD. We are mostly interested in the case of narrow distributions corresponding to small  $\alpha$ . In this limit, one can calculate the moments of the distribution function to the lowest order in  $\alpha$  rather accurately and obtain  $N_n = \langle N \rangle = N_0(1 - (3/2)\alpha)$ ;  $\langle \delta N^2 \rangle = N_0^2 \alpha^2 (12/\pi^2)(-\ln \alpha - (3\pi^2/16)) - 1 + 1/2 \ln 4 + 1/6 + 2/45 + 5/612 + \dots \approx N_0^2 \alpha^2 (-1.22 \ln \alpha - 2.35)$ .



**Figure 2.** Chain length distribution density for different values of the parameter  $\alpha = \Delta H/H_0$  (shown in the figure).  $N_{\max}$  is the cutoff degree of polymerization.

Numerical calculations show that these expressions are quite satisfactory up to  $\alpha = 0.1$ .

### Characteristics of the Polydisperse Brush

To exploit or knowledge of all of the characteristics of the original brush, we express variables  $(N_0, \rho_0, \alpha)$  through the parameters of the new polydisperse brush  $(N_n, \rho, q)$ , where  $q = N_w/N_n - 1 = \langle \delta N^2 \rangle / \langle N \rangle^2$  is the polydispersity parameter characterizing the relative width of the MMD:

$$\alpha \approx \left( \frac{q}{0.61 \ln(1/q) - \text{const}} \right)^{1/2} \approx Cq^{1/2} \quad (2)$$

$$N_0 \approx N_n(1 + 3/2\alpha) \quad (3)$$

$$\rho_0 = \rho(1 - \alpha^2)^{-3/2} \quad (4)$$

The cutoff chain length  $N_{\max}$  for the distribution function (eq 1) is given by  $N_{\max} \approx N_n(1 + (3\pi - 4/2\pi)\alpha)$ . In eq 2 we have neglected logarithmic corrections to the main power factor, treating them as constants; the value of  $C$  is roughly 0.5 for  $\alpha$  in the range 0.001–0.05. Equations 2 and 3 are valid in the limit of small  $\alpha$ . In most cases we shall still use  $\alpha$  as an independent parameter to provide a wider range of validity to the formulas derived.

The segment density profile  $\phi(x)$  of the polydisperse brush is obtained from the initial brush profile by a simple shift  $\phi(x) = \phi_0(x + \Delta H)$  and is given by

$$\phi(x) = \frac{2}{3} \left( \frac{\pi}{2} \right)^{2/3} \rho^{2/3} \{ 1 - [(1 - \alpha)x/H + \alpha]^2 \} \quad 0 \leq x \leq H \quad (5)$$

where  $x$  is the coordinate normal to the grafting plane and the segment length is taken as a unit length.

The height of the brush is

$$H = H_0 - \Delta H \approx (2/\pi)^{2/3} \rho^{1/3} (1 + \alpha/2) N_n \quad (6)$$

It follows from eq 6 that  $H$  can be written as  $H = H_m(1 + \delta)$ , where  $H_m$  is the height of a monodisperse brush formed by chains of length  $N = \langle N \rangle$  grafted with the same surface density  $\rho$ . Polydisperse brush is higher than the equivalent monodisperse one, the relative increment  $\delta$  being  $\delta = \alpha/2 \sim q^{1/2}$ . This result agrees qualitatively with the calculation by Milner<sup>4</sup> for the case of a "top-hat"

distribution which gave  $\delta = 3^{1/2}/2q^{1/2}$ . The scaling law  $\delta \sim q^{1/2}$  apparently does not depend on the particular form of MMD in the limit of narrow distributions.

The self-consistent potential  $\mu$  is also obtained by a simple shift and in the case of a good solvent is given by

$$\mu(x)/kT = \frac{3\pi^2}{8N_0^2} \left( \frac{H^2}{(1-\alpha)^2} - \left( x + \frac{\alpha H}{1-\alpha} \right)^2 \right) \quad (7)$$

or to the lowest order in  $\alpha$

$$\mu(x)/kT = \text{const} - \frac{3\pi^2\alpha H}{4N_n^2} x - \frac{3\pi^2(1-3\alpha)}{8N_n^2} x^2 \quad 0 \leq x \leq H$$

### Behavior of Individual Chains

To discuss the behavior of an individual chain in the brush, we consider the density distribution  $G(\mathbf{h}, N)$  for the end-to-end vector  $\mathbf{h}$  of the chain of length  $N$  in the presence of the potential  $\mu(x)$ . Function  $G$  is governed by an equation<sup>11</sup>

$$\frac{\partial G(\mathbf{h}, N)}{\partial N} = \frac{1}{6} (\nabla^2 - \mu(x)/kT) G(\mathbf{h}, N) + \delta(\mathbf{h}) \delta(N) \quad (8)$$

having the same structure as the Schroedinger equation for the Green function of the quantum particle in the potential  $\mu(x)$ .<sup>11</sup> We shall take advantage of the parabolic nature of the potential (eq 7) and use a well-known expression for the Green function of a harmonic oscillator<sup>12</sup> with mass  $m$  and frequency  $\omega$ . Restricting ourselves to a simple one-dimensional model corresponding to the  $x$  axis and making proper substitutions ( $\hbar \rightarrow 1$ ;  $m \rightarrow 3$ ;  $t \rightarrow N/i$ ;  $\omega \rightarrow i\pi/2N_0$ ) we get<sup>13</sup>

$$G(h_x, N) = A \exp \left( - \frac{3\pi}{4N_0 \tan(\pi N/2N_0)} \left( h_x - \frac{\alpha H [1 - \cos(\pi N/2N_0)]}{(1-\alpha) \cos(\pi N/2N_0)} \right)^2 \right) \quad (9)$$

where the normalizing constant  $A$  depends on  $N$  but does not depend on  $h_x$ . We have used parameters  $\alpha$  and  $N_0$  for the sake of generality, so that the validity of eq 9 is not restricted by the condition  $\alpha \ll 1$  (one can always go back easily to  $N_n$  and  $q$ ).

The analysis of the asymptotic behavior (at  $\alpha \ll 1$ ) of the first and second moments of the distribution (eq 9) is rather close to that in ref 5 for a short admixture chain amid the chains of a monodisperse brush. The quadratic term of the potential modifies the elastic modulus of chains and thus affects both their susceptibility to stretching by the constant component of the total force and the average magnitude of chain size fluctuations. Note that this term is the same as in the initial monodisperse brush consisting of chains of length  $N_0$ . The basic reason underlying the strong effects discussed in this paper is that for the chain of length  $N_0$  the quadratic term exactly cancels its Gaussian elasticity so that the conformation corresponds to the middle of the coil-stretch transition.<sup>5</sup> The chains of the polydisperse brush under consideration are shorter, but in the case of small  $q$  they are still close to  $N_0$  and hence are able to display critical type of behavior.

A typical chain with  $N = N_n = N_0(1 - 3\alpha/2)$  will have mean-square size fluctuations  $\langle \delta h_x \rangle^2 = \langle (h_x - \langle h_x \rangle)^2 \rangle$  given by

$$\langle \delta h_x \rangle^2 \sim N q^{-1/2} \quad \text{if } 1 \gg q \gg N_n^{-2} \rho^{-4/3}$$

$$\langle \delta h_x \rangle^2 \sim N^2 \rho^{2/3} \quad \text{if } q \ll N_n^{-2} \rho^{-4/3}$$

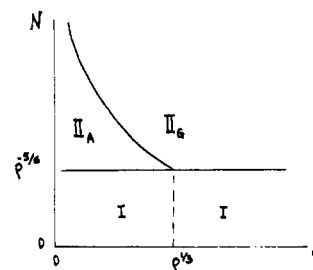


Figure 3. Diagram of the asymptotic regimes of the individual chain behavior in a polymer brush;  $q = N_w/N_n - 1$  is the polydispersity parameter, and  $N$  is a typical chain length. See Table I for scaling laws.

Here we have used the polydispersity parameter  $q = N_w/N_n - 1$  ( $q \sim \alpha^2$ ) and omitted numerical coefficients of order 1.

It is clear that for  $1 \gg q \gg N_n \rho^{-4/3}$  the elastic constant of the chain in the presence of the quadratic stretching field is effectively decreased by the factor  $q^{1/2}$  compared with the unperturbed value  $K_0 \sim 1/N_n$ .

The average normal component of the end-to-end distance for  $N = N_n$  obtained from eq 9 is, in the limit of small  $\alpha$ ,  $\langle h_x \rangle = 4H/3\pi$ . It could be estimated alternatively as  $\langle h_x \rangle \sim f_{tot}/K_{eff} \sim (Hq^{1/2}N_n)/(q^{1/2}/N_n) \sim H$ , where  $f_{tot} \sim N_n \partial \mu_{lin} / \partial x \sim \rho^{1/3} q^{1/2}$  is the total constant component of the stretching force per chain and  $K_{eff} \sim K_0 q^{1/2}$  is the modified elastic constant of the chain. With the increase in polydispersity, the constant component of the stretching force becomes more and more important, while elastic constant  $K_{eff}$  becomes closer to that of an isolated chain. For large  $q \sim 1$ , a chain in a brush behaves like an isolated chain stretched by a constant force.

For small  $q$ ,  $q \ll N_n^{-2} \rho^{-4/3}$ , the fluctuational behavior and the average stretching are governed by the fact that the chain is actually confined inside the brush of thickness  $H$  so that both  $\langle h_x \rangle$  and  $\delta h_x$  always remain of order  $H$  (see also refs 5 and 14).

### N-q Diagram

We summarize the possible types of chain behavior in a polymer brush by constructing a diagram in the coordinates  $(N, q)$ , where  $N$  is a typical chain length for a given MMD (see Figure 3). Note that we consider only the case of relatively narrow chain length distribution with all of the moments being finite. There are three regions corresponding to different asymptotic regimes. The boundaries between the regimes do not mean that there are sharp transitions but rather indicate the positions of the crossover regions.<sup>15</sup> Some examples obtained by numerical calculations will be shown in the next section.

Regime I ( $N^{6/5} \rho < 1$ ) corresponds to the system of nonoverlapping coils grafted onto a plane. The mean-square size and size fluctuations of a typical chain are  $\langle h_x \rangle^2 \sim \langle \delta h_x \rangle^2 \sim N^{6/5}$ .

Regime II\_A ( $N^{6/5} \rho > 1$ ;  $q < N^2 \rho^{-4/3}$ ) corresponds to a well-developed effectively monodisperse brush with  $\langle h_x \rangle^2 \sim H^2 \sim N^2 \rho^{2/3}$  and anomalous  $N$  dependence of chain size fluctuations  $\langle \delta h_x \rangle^2 \sim N^2 \rho^{2/3}$ .

Regime II\_G ( $N^{6/5} \rho > 1$ ;  $q > N^2 \rho^{-4/3}$ ) corresponds to a polydisperse brush. Here  $\langle h_x \rangle^2 \sim N^2 \rho^{2/3}$  as in regime II\_A, but the mean-square chain fluctuations  $\langle \delta h_x \rangle^2 \sim N q^{-1/2}$  are Gaussian with respect to their  $N$  dependence, although enhanced by the factor  $q^{-1/2}$ . They do not depend on the surface coverage  $\rho$  in this regime.

**Comparison with Numerical Calculations.** To verify and illustrate the asymptotic results of the analytic theory, we have performed numerical calculations for a

lattice model by exactly repeating the trick described under Model Molecular Mass Distribution. The model used was that of a random walk on a simple cubic lattice in the presence of a self-consistent field. The general method and a detailed description of the model are given in refs 16 and 17. The calculations were performed only for the case of a good solvent. First, the self-consistent segment density and the corresponding potential profiles were calculated for monodisperse brushes with  $N_0 = 100, 200, 300, \text{ or } 400$  and  $\rho = 0.03$  or  $0.15$ , the condition of strong overlapping being satisfied. Then, characteristics of shorter chains of length  $N$  attached to a ghost plane at distance  $\Delta H$  from the original grafting plane were computed. For each set of parameters ( $H_0, \Delta H, N_0$ ),  $N$  was taken equal to the number average  $N_n$  of a corresponding MMD given by eq 1. The results were expressed in terms of the parameters  $N, \rho$ , and  $q$  of the new brush.<sup>18</sup>

Let us consider separately dependences of the chain characteristics on the molecular mass and on polydispersity. First, we keep increasing the average molecular mass of the chains forming a brush, with the surface coverage  $\rho$  and the polydispersity parameter  $q \ll 1$  being fixed. This corresponds to moving along the  $N$  axis on the diagram (Figure 3). The mean-square size of a typical chain,  $\langle h^2 \rangle$ , depends only weakly on the polydispersity.<sup>2-4</sup>

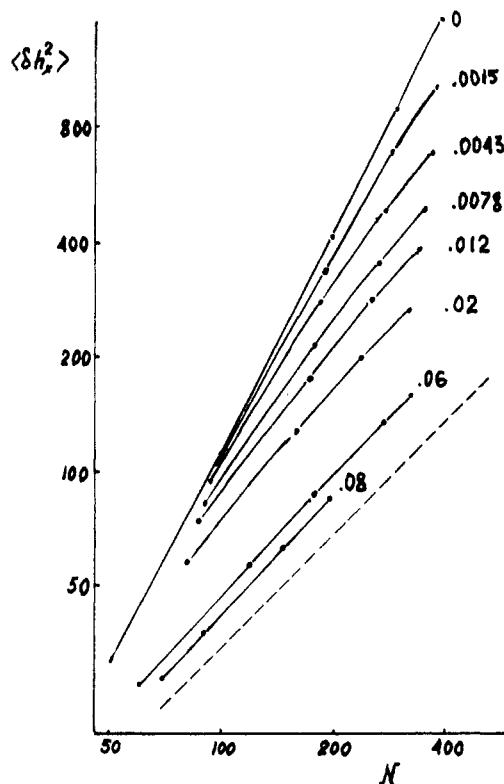
$$\langle h_x^2 \rangle \sim N^{6/5} \quad N < \rho^{-5/6} \text{ (regime I)}$$

$$\langle h_x^2 \rangle \sim N^2 \rho^{2/3} \quad N > \rho^{-5/6} \text{ (regimes II}_A \text{ and II}_G \text{)}$$

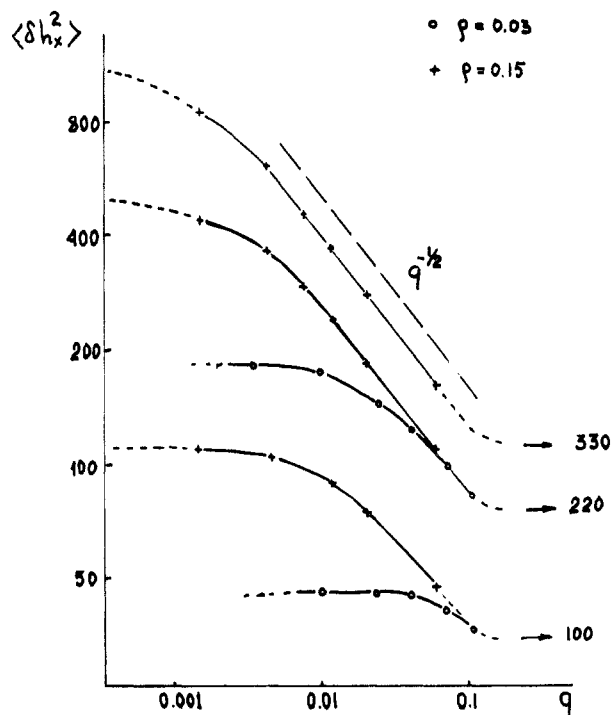
The fluctuational behavior, however, is more intricate. For a completely monodisperse brush ( $q = 0$ ),  $\langle \delta h_x^2 \rangle \sim H^2$  and thus has exactly the same scaling behavior.<sup>6-8,17</sup> If the distribution has a non-zero but small enough width,  $0 < q \ll \rho^{1/3}$ , we pass consecutively regimes I, II<sub>A</sub>, and II<sub>G</sub> with the corresponding power laws  $\langle \delta h_x^2 \rangle \sim N^{6/5}$ ,  $\langle \delta h_x^2 \rangle \sim N^2 \rho^{2/3}$ , and  $\langle \delta h_x^2 \rangle \sim Nq^{-1/2}$ , and so the governing exponent should change nonmonotonically with increasing  $N$ . Finally, if the inhomogeneity parameter is large enough,  $q \gg \rho^{1/3}$ , we miss regime II<sub>A</sub> and there is no anomalous  $N$  dependence of the fluctuation magnitude. (Smaller effects due to the boundary conditions may somewhat complicate the crossover behavior.)

Figure 4 shows the numerical results for the case of rather dense well-developed brushes. One can clearly see the change from  $N^2$  to  $N$  dependence of the mean-square end-to-end fluctuation with increasing chain length, as we pass from regime II<sub>A</sub> to regime II<sub>G</sub>, which can be detected even for very small  $q$ . The crossover shifts to smaller  $N$  with the increase in polydispersity. We do not see the anomalous regime II<sub>A</sub> even for  $q = 0.06-0.08$ , though it might still exist at  $N < 50$ . In this case it should be quite narrow, and we anticipate it to disappear completely for even larger  $q$ . (The numerical results for larger  $q$  are not presented, since the condition of strong stretching was satisfied only marginally for these samples, and the validity of the trick employed was not evident.)

Let us now take several polymer brushes with the same average chain length  $N$  and grafting density  $\rho$  ( $N^{6/5}\rho \gg 1$ ) but with different (though rather small) degrees of polydispersity  $q$ . This will correspond to a horizontal section of the  $N$ - $q$  diagram traversing regions II<sub>A</sub> and II<sub>G</sub>. As we move toward more narrow distributions ( $q \rightarrow 0$ ) the end-to-end distance fluctuations for a typical chain increase according to the power law  $\langle \delta h_x^2 \rangle \sim Nq^{-1/2}$  (regime II<sub>G</sub>) until we get into regime II<sub>A</sub>, where they saturate at the level characteristic of a monodisperse brush  $\delta h_x \sim N\rho^{1/3}$ . Figure 5 illustrates this behavior, and one can see that in



**Figure 4.** Log-log plot of the mean-square size fluctuation  $\langle \delta h_x^2 \rangle$  for a chain in a brush with the surface coverage  $\rho = 0.15$  vs the degree of polymerization,  $N$ , for different degrees of polydispersity,  $q$  (shown in the figure). For comparison,  $\langle \delta h_x^2 \rangle = N/3$  for a chain stretched by the ends with a constant force within the range of Gaussian elasticity is also given (dashed line).



**Figure 5.** Log-log plot of the mean-square size fluctuation  $\langle \delta h_x^2 \rangle$  for a chain in a brush vs the polydispersity parameter  $q = N_w/N_n - 1$  for different chain lengths,  $N$  (shown in the figure), and two different surface coverages  $\rho$ . At small  $q$ , the curves are extrapolated to the limiting values for monodisperse brushes, at large  $q$  to that for a chain stretched with a constant force.

regime II<sub>G</sub> chain fluctuations practically do not depend on the grafting density  $\rho$ , though the width of the II<sub>G</sub> region is much smaller for  $\rho = 0.03$ .

Table I  
Regimes of Asymptotic Behavior for the Chain Size and Size Fluctuations

	I	II <sub>A</sub>	II <sub>G</sub>
$\langle h^2 \rangle$	$N^{2\nu}$	$N^2 \rho^{(1-\nu)/\nu}$	$N^2 \rho^{(1-\nu)/\nu}$
$\langle \delta h_x^2 \rangle$	$N^{2\nu}$	$N^2 \rho^{(1-\nu)/\nu}$	$N q^{-1/2}$
Equations of Boundaries			
I-II		$N \sim \rho^{-1/2\nu}$	
II <sub>G</sub> -II <sub>A</sub>		$N \sim q^{-1/2} \rho^{(\nu-1)/\nu}$	

**Solvent Quality Effects.** Previous results can be readily generalized for the brush in a  $\Theta$  solvent or in a precipitant; the molten state may be treated as an extreme case of the latter system. The trick we have used to obtain a convenient form of MMD works as well, and the basic eqs 2 and 3 are still valid (some numerical coefficients change slightly but the scaling dependencies hold). The change in the solvent quality leads to the change in  $\rho$  dependence of both the average chain size and the size fluctuation. Thus, the diagram will retain its general form (see Figure 3), though the asymptotic behavior of  $\langle h^2 \rangle$  and  $\langle \delta h_x^2 \rangle$ , as well as the positions of the boundaries between different regimes, changes somewhat (see Table I). As usual, we take  $\nu = 3/5$  for a good solvent,  $\nu = 1/2$  for a  $\Theta$  solvent, and  $\nu = 1/3$  for a precipitant. The "triple point", i.e., the crossing of two boundaries (see Figure 3), corresponds to  $q \sim \rho^{2-1/\nu}$ . This transforms back to  $q \sim \rho^{1/3}$  in the case of a good solvent, but with decreasing solvent quality the position of the triple point shifts to larger  $q$  ( $q \geq 1$ ). The validity of the present consideration is limited to small  $q$ , and there is no point in discussing the details of the diagram in the region  $q > 1$ . Still, we can make a qualitative conclusion that with  $\Theta$  or precipitant conditions (or in the melt) one necessarily encounters a regime with anomalous fluctuation growth in the experiment with increasing  $N$  (with both  $q < 1$  and arbitrary  $\rho$  fixed). This corresponds to moving along a vertical section of the  $q$ - $N$  diagram. Provided  $q \ll 1$ , the triple point corresponding to  $q \geq 1$  will be far to the right from the section, and one has to cross region II<sub>A</sub>.

## Discussion

In a previous paper<sup>5</sup> we argued that large-scale chain fluctuations in a monodisperse brush grafted onto a planar surface are of critical nature and correspond to the middle of the coil-stretch transition. This notion extends to the system under consideration as well. Thus, the power dependence of  $\langle \delta h_x^2 \rangle$  on  $q$  for regime II<sub>G</sub> is analogous to fluctuation growth in the vicinity of a second-order phase transition in the mean field picture, and decreasing the polydispersity parameter  $q$  is analogous to approaching the critical temperature. A more rigorous analogy is between  $\alpha \sim q^{1/2}$  and  $|T - T_c|/T_c$  (see ref 5 for a more detailed discussion).

It is clear from Figure 5 that both for rather loose ( $\rho = 0.03$ ) and especially for denser brushes ( $\rho = 0.15$ ) with chains as long as 200–300 segments even extremely small polydispersity with  $q \sim 10^{-2}$ – $10^{-3}$  may affect fluctuational and, hence, relaxational properties very significantly. This should be possible to verify, for example, by measuring low-frequency dielectric relaxation for a system containing end-attached chains with a non-zero component of a dielectric moment along the end-to-end vector, such as poly(propylene oxide)<sup>19</sup> or *cis*-polyisoprene.<sup>20,21</sup>

The relaxation of this low-frequency dielectric mode is governed by the relaxation of the vector  $\mathbf{h}$ .<sup>19</sup> In the absence of the entanglement effects, its characteristic time  $\tau$  is essentially determined by the magnitude of the end height

fluctuation for a chain in the brush:<sup>5</sup>  $\tau \sim \zeta \langle \delta h_x^2 \rangle / kT$ , where  $\zeta$  is the friction coefficient for the large-scale chain motions. For a free-draining Rouse model  $\zeta = N\zeta_0$ , with  $\zeta_0$  being the friction coefficient of a segment. Taking into account the (screened) hydrodynamic interactions in a brush with a moderate density, we obtain in the simplest approximation<sup>5</sup>  $\zeta \sim N\rho^{1/3}\zeta_0$ . In both cases we have  $\tau \sim N\langle \delta h^2 \rangle$ , which gives anomalous relaxation  $\tau \sim N^3$  in regime II<sub>A</sub> and a modified Rouse relaxation  $\tau \sim N^2 q^{-1/2}$  in regime II<sub>G</sub>. It is interesting to note that, for a fixed small enough polydispersity parameter,  $0 < q \ll \rho^{1/3}$ , increasing the average molecular mass will yield a nonmonotonous change in the exponent  $\beta$  governing the molecular mass dependence of  $\tau \sim N^\beta$ . It starts from  $\beta = 9/5$  corresponding to self-avoiding single coil dynamics in regime I, then changes to  $\beta = 3$  for the anomalous relaxation in the effectively monodisperse brush (regime II<sub>A</sub>), and finally comes to  $\beta = 2$ , characteristic of Rouse relaxation in regime II<sub>G</sub>.

A question arises if the relaxational behavior discussed above could be ever observed, since the interference of the entanglement effects smears the whole picture. The above consideration of chain dynamics is based on the simple formula  $\tau \sim \langle \delta h^2 \rangle \zeta$  which relates relaxation time to the equilibrium mean-square fluctuation. The equilibrium characteristics do not depend on the motion mechanism, but the relationship cited breaks down with the onset of reptation. The onset of reptation as a dominant mechanism of large-scale relaxation in polymer melts<sup>22</sup> is supposed to occur as the number of chain segments  $N$  becomes larger than  $N^* \sim 10^2$ . The dependence of  $N^*$  on the polymer concentration for the case of semidilute and concentrated solutions is still not clarified. It seems that brushes with moderately dense grafting ( $\rho \sim 10^{-1}$ ) immersed in good solvent are unlikely to manifest significant entanglement effects at least for  $N \lesssim 10^3$  (this tentative estimate is based on the results of refs 23 and 24). Hence, we have good hope that, for brushes with moderate surface coverage and intermediate molecular weights, one would be able to observe a very unusual slowing down of the large-scale relaxation with the decrease in polydispersity.

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## References and Notes

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- In deriving eq 8 we have not taken into account the influence of the impenetrable plane at  $x = 0$  and the fact that  $\mu(x) = 0$  for  $x \geq H$ . The first factor does not change the qualitative effects considered in the present paper, even in the absence of

the linear stretching term in  $\mu(x)$ . With the constant component of the stretching force hindering the return of the free chain end to the grafting plane, this influence should be even less significant. The second factor is unimportant if  $N$  is not too close to  $N_0$ . In the case of an essentially monodisperse layer it is important and limits the fluctuations of the end-to-end distance to be of order  $H$  (see discussion in ref 5).

- (14) Milner, S. T.; Wang, Z. G.; Cates, M. E. *Macromolecules* **1989**, *22*, 489.
- (15) The asymptotic regimes match along the boundaries I-II<sub>A</sub> and II<sub>A</sub>-II<sub>G</sub>, but there is a certain discrepancy at the I-II<sub>G</sub> boundary. There is no matching problem with the average size of the chain, but expressions for the fluctuations differ by the factor  $(q/\rho^{1/3})^{1/4}$ . This is not totally surprising since we have used a self-avoiding chain model for regime I and the SCF model of a Gaussian chain for regime II<sub>G</sub>. One should rather be surprised that these asymptotics do match at the I-II<sub>A</sub> boundary (which is in fact due to the anomalous non-Gaussian behavior in the II<sub>A</sub> regime). In the region of validity of the present consideration the factor  $(q/\rho^{1/3})^{1/4}$  is, however, always close to 1 on the I-II<sub>G</sub> boundary, since the theory of "parabolic" brushes is only correct for moderately small  $\rho$  and at the same time  $q$  should satisfy the condition  $1 \gg q \geq \rho^{1/3}$ .
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- (18) Strictly speaking, this is not an independent numerical SCF calculation for a model polydisperse brush. One should rather consider it as an extension of the analytical investigation presented above which provides an accurate treatment of the boundary condition at the outer edge of the brush, does not use the assumption of Gaussian elasticity, and gives quantitative results. In the calculation described, one cannot simply start treating the ghost plane as impenetrable, since the self-consistency of the density profile will be somewhat violated. Again, we anticipate the results to be correct in the strong stretching limit, when the contribution of chains going back, under the ghost plane, becomes negligible.
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