

Linear gradient copolymer melt brushes

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I consider a brush of gradient polymers, with the chains anchored at their pure *A* ends with the chemical composition changing linearly along the chain up to the untethered chain tips whose composition is pure *B*. Demixing of the *A* and *B* monomers results in the creation of a thermally-controllable zone from which free ends are excluded. For high temperatures, the zone is small and located near the grafting surface, but for lower temperatures the zone extends throughout the layer, giving a physical manifestation of an Alexander brush. This conclusion is supported by both scaling and numerical self-consistent field calculations. © 2003 American Institute of Physics. [DOI: 10.1063/1.1538603]

I. INTRODUCTION

A particularly fruitful strategy for creating complicated three-dimensional heterostructures in polymeric systems is to embed in the primary structure of the polymers some chemical regularity, and to take advantage of collective self-assembly effects.¹ The classic example is that of the block copolymers.² Here, care is taken to implant large blocks, that is continuous runs, of one type of monomer alternating with another along the chain. Wonderful three-dimensional patterns composed of two different components are possible.³ In going from diblock copolymers to *ABC* triblock copolymers, even more interesting patterns emerge in equilibrium.⁴ Instead of increasing the chemical complexity along the chain by including more and more varieties of monomers, a way to increase the complexity of the equilibrium patterns is to couple the pattern to an external field, thus offering a degree of control over the pattern, as well as enriching the ultimate behavior. Either through controlling wetting interactions,⁵ by the imposition of static thermal gradients,⁶ or through the application of electromagnetic fields,⁷ increasingly complex patterns, with increasingly finer control, are being achieved regularly.

The control with which monomers can be ordered along a polymer has grown tremendously as well in the past few years, bringing a class of “gradient” or “taper” polymers into focus. These polymers are synthesized by controlling the relative population of *A* and *B* monomers during synthesis, so that any particular statistical pattern for the arrangement of the monomers on the polymer is quite easy to design.⁸ Block copolymers are an extreme form of these gradient polymers, a diblock being synthesized by imposing that the probability of adding an *A* monomer be zero until after a certain point at which it becomes unity. Thus, the composition along the chain can be designed to vary smoothly (in a statistical sense), so that the composition is “tapered” or has a gradient. In what follows, the chains have a linear gradient, so that the fraction of *A* monomers varies linearly from the pure *A* end of the chain towards the pure *B* end. It should be noted that the opposite extreme, that of the random

copolymer,^{9–11} is also possible in this scheme, so that the probability of adding an *A* or a *B* monomer stays constant during synthesis. Even small variations in the overall concentration of these monomers in the bulk or a small difference in the monomer reactivities is sufficient to cause a composition “creep” during synthesis that can result in random copolymers with a slight composition drift.^{12,13} These accidentally produced taper copolymers offer many advantages in strengthening polymer blends at their weakest point, their interfaces.

In most respects, these gradient copolymers behave as block copolymers made of two more compatible monomers.^{8,14} While there are some differences between the block copolymer and the gradient copolymer microsegregation diagrams, the overall scheme is the same. *A*-rich domains are surrounded by *B*-rich domains, and a variety of geometries for the packing of the domains is possible, including bicontinuous packings.

Gradient copolymers can, in one very interesting respect act very differently from block copolymers, and that is when they are employed to create a polymer brush.¹⁵ These end-confined layers can be constructed by grafting each polymer by one end at a hard, impermeable substrate. In the diblock case, I envision a grafting where each *A* block is tethered to the surface, so that the *B* blocks are free to stretch away from the surface. As the temperature is lowered, the incompatibility of the *A* and *B* blocks drives a microsegregation in the layer, so that a layer of pure *A* forms at the substrate, and a layer of pure *B* forms at the extreme edge of the brush. The *A* blocks necessarily form bridging strands extending from the grafting surface all the way to the *AB* interface. The *A* layer is thus a physical manifestation of the Alexander brush,^{16,17} while the *B* layer is a standard polymer brush.^{18,19} If, as has proven useful, control over the free ends of the brush is needed, then one would see a sequence of events in the diblock case in which the free *B* ends are distributed throughout the layer at high temperatures, with a distribution highly peaked at the outer surface. As the temperature is lowered, microsegregation in the layer causes a spontaneous expulsion of the *B* ends from the growing Alexander-type *A*

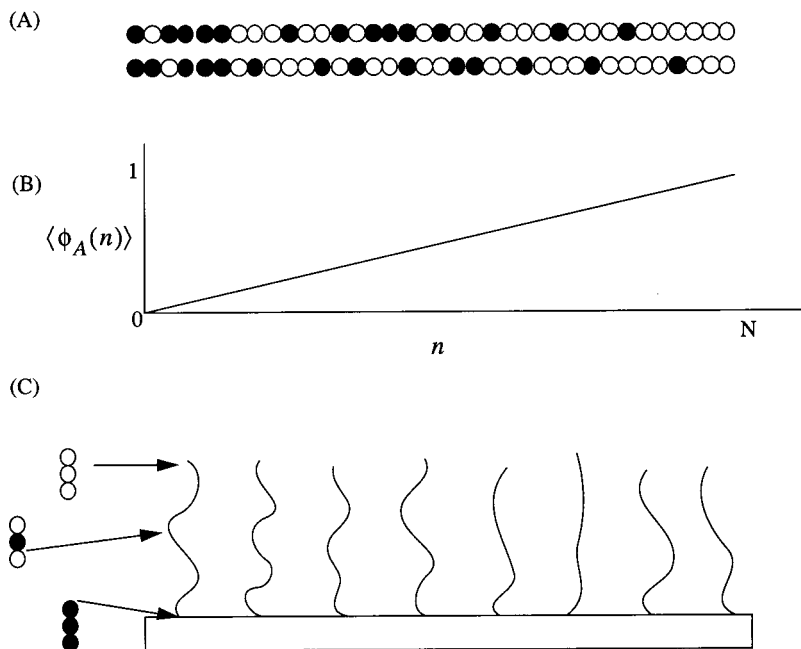


FIG. 1. Schematic. (A) Two typical sequences for an $N=40$ linear gradient copolymer, and (B) the average composition along the chain. (C) The brush is arranged so that the typical monomer sequence along the chain is pure A at the grafting surface, evenly distributed between A and B in the middle of the chains, and purely B at the ungrafted, “free tips.”

layer near the grafting surface. Further reduction in temperature has no effect on the location and distribution of the B ends. Given that it is possible to engineer terminal end groups with an almost limitless specificity of interaction with a targeted molecule via organic ligand interactions, more control than this over the distribution of the chain tips may be desirable.

Gradient copolymers, on the other hand, offer a novel control over the location and enrichment of the polymer free ends by controlling temperature. The gradual shift in composition along the chain smoothes out the distribution of A monomers in the brush, allowing a continuous control over both the width of zone from which free-ends are expelled, and the enrichment of the tips at the free surface of the brush. As with many surface applications of polymers, the critical question can often be framed as “where are the free ends?” The answer to this question is of critical importance in considering dendrimers,^{20,21} creating specific smart surfaces for biological assays and cell adhesion,²² controlling the surface tension of polymer blends,²³ and in controlling the surface orientation of lamellar stripes in thin films.²⁴

The paper is organized as follows: First, I describe a simple scaling model which predicts the onset of the end-exclusion zone for linear gradient brushes. Next, I describe how the linear gradient can be modeled in a numerical lattice self-consistent field (SCF) model.²⁵ I then compare the behavior of the end distribution in both the gradient and diblock brush as a function of the incompatibility of the A and B monomers via the Flory–Huggins χ interaction parameter. I then offer a few observations and make my conclusions.

II. SCALING MODEL

The properties of the diblock copolymer brush, where each polymer is grafted by its A tip are well understood, in

many models. Here, I focus on the new features introduced when the chains in the brush are gradient copolymers.

So, let σ polymers per unit area be grafted at an impenetrable, smooth surface located at $z=0$. The copolymers have N segments in all, and the probability that the n th monomer is of type A is given by

$$p_A(n) = \frac{n}{N}. \quad (1)$$

The $n=0$ monomer is free to explore the volume $z>0$, while the $n=N$ monomer is grafted to $z=0$, as in Fig. 1. Thus, the grafted monomers are all A monomers, the extreme tips of the copolymers are entirely B monomers, and there is a linear relationship between monomer number n and the average composition along the chain. The monomers on the brush fill space densely,

$$h = \sigma N a^3, \quad (2)$$

where a^3 is the volume occupied by a single monomer. For the purposes of this argument, the composition of the chains is quenched, but I will ignore the actual quenched sequence of monomers on each individual chain in favor of a coarse-grained description depending only on the average composition of all the monomers with the same monomer number.

Consider first the athermal situation, in which the Flory–Huggins interaction parameter, χ between A and B monomers vanishes. When the brush height, h , satisfies

$$aN^{1/2} \ll h \ll aN, \quad (3)$$

where a is the typical monomer size, the structure of the brush is well known.^{18,19} Given that a single polymer in the brush has its free end located at z_0 , the average locations of all the other monomers on the chain are known,

$$z(n) = z_0 \cos \frac{\pi n}{2N}. \quad (4)$$

In equilibrium, the number of free ends per grafting area located between z_0 and $z_0 + dz$ is defined to be $\xi(z_0)dz$ and is known to be

$$\xi(z_0) = \frac{\sigma}{h} \frac{z_0}{\sqrt{h^2 - z_0^2}}, \quad (5)$$

properly normalized so that $\int_0^h dz \xi(z) = \sigma$. This distribution of ends ensures the melt condition is satisfied self-consistently, so that at each height z in the layer the monomers from all chains with $z < z_0$ just fill all the available space. The partial volume fraction, $\phi(z; z_0)$, is defined to be the volume fraction taken up at the position z by monomers on a test chain whose free end is held at z_0 , and is given by

$$\phi(z, z_0) = a^3 \sigma \frac{dn}{dz}, \quad (6)$$

so that

$$\phi(z) = \int_z^h dz_0 \xi(z_0) \phi(z; z_0) \equiv 1. \quad (7)$$

Thus, the volume fraction of monomers within the brush is held constant, independent of z .

This implies that there are considerable gradients in the A (and hence B) monomer volume fractions. To calculate the athermal A monomer volume fraction, it is necessary to modify Eq. (7) slightly,

$$\phi_A(z) = \int_z^h dz_0 \xi(z_0) \phi_A(z; z_0), \quad (8)$$

where

$$\phi_A(z; z_0) = \phi(z; z_0) \frac{2}{\pi} \arccos \frac{z}{z_0}, \quad (9)$$

for a gradient brush and

$$\phi_A(z; z_0) = \phi(z; z_0) \quad \text{when } z < \frac{z_0}{\sqrt{2}}, \quad (10)$$

and vanishes otherwise, for an A -grafted diblock copolymer brush. I have used explicitly the probability, Eq. (1) for the A monomers as a function of monomer number, and a discrete distribution for the diblock brush. The volume fraction of A monomers thus determined is shown in Fig. 2, along with the distribution of monomers expected for a diblock copolymer brush for comparison.

In the gradient copolymer case, the spontaneous athermal distribution of A monomers is quite close to what it would be in the limit of very strongly repulsive AB interactions,

$$\phi_A(z) = 1 - \frac{z}{h} \quad \text{as } \chi \rightarrow \infty. \quad (11)$$

To calculate the extent of the B end-exclusion zone, I will initially assume that independent of χ , the ϕ_A profile is exactly that given in Eq. (11). I then determine conditions under which a chain whose composition is governed by Eq. (1) will spontaneously extend itself over the entire brush height, h .

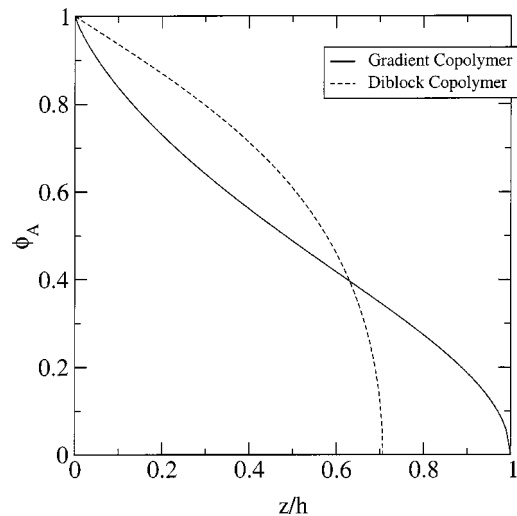


FIG. 2. ϕ_A for athermal brushes. A monomer concentration profiles for $\chi = 0$ for a linear gradient brush (solid line) and a diblock copolymer (dashed line).

First, assume that all of the chains in the brush and the test chain are constrained to lay on the vertices of a cubic lattice. When χ is sufficiently large so that the end-exclusion zone extends throughout the layer, all of the brush chains have

$$z(n) = h \left(1 - \frac{n}{N} \right). \quad (12)$$

That is, the brush chains bridge the gap from $z=0$ to $z=h$, so that the brush is in reality an Alexander brush.^{16,17} I will find the lowest value for χ which will satisfy this. Let us hold a chain identical to the brush chains so that

$$z(n) = \frac{1}{2}(h + \Delta z) - \frac{n}{N} \Delta z. \quad (13)$$

That is, the test chain is stretched uniformly from $h - \Delta z/2$ to $h + \Delta z/2$. The free energy to maintain the test chain in this conformation is

$$F_{\text{test}} = S_{\text{test}} + U_{\text{test}}. \quad (14)$$

The entropy cost to maintain the chain in this conformation is just the Gaussian elastic energy,

$$S_{\text{test}} = \frac{3}{2} \frac{\Delta z^2}{a^2 N}. \quad (15)$$

The enthalpic cost to maintain the test chain in this conformation (relative to the pure A and B substances as references) is

$$U_{\text{test}} = \chi \sum_{n=0}^N f_A(n) \langle \phi_B(z(n)) \rangle + f_B(n) \langle \phi_A(z(n)) \rangle. \quad (16)$$

Here, $f_A(n)$ is the probability that the n th monomer on the chain is an A monomer, and the angled brackets represent a nearest-neighbor contact sum on a simple cubic lattice,

$$\langle Y(z) \rangle = \frac{1}{6} [Y(z-1) + 4Y(z) + Y(z+1)]. \quad (17)$$

Thus, U_{test} is simply counting all of the pairwise $A-B$ contacts for the test chain, with each contact costing χ units of free energy (in natural thermal units where Boltzmann's constant times temperature, $k_B T = 1$). For any quantity that varies linearly in z , this contact fraction is particularly simple,

$$\langle a + bz \rangle = a + bz. \quad (18)$$

Thus, it is a simple matter to calculate U_{test} ,

$$U_{\text{test}} = \chi \int_0^N dn \left(\frac{h - \Delta z}{2h} + \frac{2\Delta z n}{hN} - \frac{2\Delta z n^2}{hN^2} \right), \quad (19)$$

where I use a continuous notion for the monomer number, n . Doing this integral allows the computation of the full test free energy,

$$F_{\text{test}} = \frac{N(h - \Delta z/3)}{2h} + \frac{3}{2} \frac{\Delta z^2}{a^2 N}. \quad (20)$$

The test chain will attain a spontaneous extension, Δz determined by $\partial F_{\text{test}} / \partial \Delta z = 0$,

$$\frac{\Delta z^*}{h} = \frac{\chi N^2 a^2}{18h^2} = \frac{1}{18} \chi \sigma^{-2} a^{-4}. \quad (21)$$

This spontaneous extension of the chain takes up the entire layer, $0 < z < h$ when $\Delta z^* = h$, or

$$\chi = \chi^* = 18\sigma^2 a^4. \quad (22)$$

It can similarly be shown that when $\chi < \chi^*$, the spontaneous end-exclusion zone in the layer spans a proportionately smaller height,

$$Z^* = \frac{\chi}{\chi^*} h = 18\chi \sigma^{-2} a^{-4} h. \quad (23)$$

The caveat here is that for $\chi \approx \chi^*$ the composition profile in the brush is linear. This is only approximately true, even for small χ , and

$$\phi_A(z) \approx 1 - \text{const. } z \log z, \quad (24)$$

for small z . Thus, there is only a rough agreement between the numerical approach below and the simple linear prediction made in Eq. (23).

III. SCF MODEL

The size of the zone from which B ends are excluded as calculated above rests on a host of assumptions that are hard to relax in an analytic calculation, e.g., it is possible to achieve a temperature low enough so that all of the chains bridge the brush layer, the A monomer profile is linear, and so on. Here, I relax all of these assumptions, and in a numerical, self-consistent manner determine the proper statistical averages over all brush-chain lattice conformations to determine numerically Z^* , the extent of the end-exclusion zone. As above, I assume that all of the chains in the system reside on a simple cubic lattice, with $z = 1$ marking the plane where each grain is grafted, and $z = L_z$ marks the extreme edge of the brush. I assume that all quantities are homogeneous in the x and y directions in this lattice, so that I only need to keep track of quantities that vary with height, z , in

the layer. Each chain thus has its N th monomer located at $z = 1$, with the rest of its monomers being played out in the region $1 \leq z \leq L_z$.

The chemical gradient along the chain can be simulated directly, through generating many random quenched sequences of monomers according to the distribution given in Eq. (1).^{8,10} While such a calculation is possible, and had proven quite successful in modeling systems consisting of random copolymers, the tack here is more coarse grained. I enforce the average composition of the n th monomer along the grafted chains by taking a suitable weighting of the Boltzmann factors for inserting an A monomer with a given frequency. So, consider the n th monomer on the chain, and the position z in the lattice. Let $U_A(z)$ be the total energy to place an A monomer at the position z in the lattice, and similarly for $U_B(z)$. Given that the n th monomer is an A monomer for a fraction of $p(n)$ of the chains, the average energy to insert the n th monomer in the layer is

$$U_n(z) = p(n)U_A(z) + (1 - p(n))U_B(z), \quad (25)$$

so that the statistical weight that should be assigned to having the n th monomer located at z should be

$$g(z; n) = \exp[-U_n(z)]. \quad (26)$$

Note that this argument keeps the probabilities with which A and B monomers actually enter the chain to be independent of the manner in which the chains are arranged on the lattice, and that this distribution of A and B monomers thus will not adjust itself to attain thermodynamic equilibrium. The average sequence distribution on the chains is quenched, although the sequence distribution I use is necessarily coarse-grained.

Given Eq. (26), it is now possible to build up the statistical weight for the chains on the lattice using the usual recursion relations of Scheutjens and Fleer.²⁵ We can build up the overall statistical weight to have one of the brush chains have its first, free, monomer at z_0 monomer by monomer. Inserting the first monomer at z_0 imposes a statistical weight,

$$G(z, z_0; 1) = g(z_0; 1) \text{ when } z = z_0, \quad (27)$$

and vanishes otherwise, where $G(z, z_0; n)$ is the unnormalized statistical weight to have the n th monomer on the chain located at z given that the first monomer is located at z_0 . The next monomer must be adjacent to the first monomer on the chain, so that the Scheutjens and Fleer scheme correctly accounts for the connectivity of polymer chains, if not their actual geometry leading to steric interactions. Inserting the second monomer gives a weight,

$$G(z, z_0; 2) = g(z; 2) \langle G(z, z_0; 1) \rangle, \quad (28)$$

where the angled brackets stand for the contact fraction introduced above. The chain can continually be built up,

$$G(z, z_0; n) = g(z; n) \langle G(z, z_0; n-1) \rangle, \quad (29)$$

with

$$G(z, z_0; N) = g(1; N) \langle G(z, z_0; N-1) \rangle \text{ when } z = 1, \quad (30)$$

and vanishes otherwise, as the N th monomer has been designated the grafted monomer.

The total free energy associated with chain conformations with the free end located at z is then

$$F(z) = \log G(1; z_0, N), \quad (31)$$

and the total entropic contribution to the free energy per surface area in the brush is

$$S = \sigma \sum_{z=1}^{z=L_z} F(z). \quad (32)$$

The enthalpic contribution to the free energy can be calculated by counting up all of the $A-B$ contacts in the brush,

$$E = \chi \sum_{z=1}^{z=L_z} \phi_A(z) \langle \phi_B(z) \rangle. \quad (33)$$

Calculating the average A monomer volume fraction is possible from a knowledge of the $G(z, z_0; n)$'s. In particular,

$$\phi_A(z) = \frac{\sum_{n=1}^N p(n) \sum_{z'=1}^{L_z} G(0, z; n) G(z, z')}{\sum_{n=1}^N \sum_{z'=1}^{L_z} g(z, n) G(1, z'; N)}. \quad (34)$$

The point of the calculation is to determine the correct form for $U_A(z)$ and $U_B(z)$ so that incompressibility is enforced,

$$\phi_A(z) + \phi_B(z) = 1, \quad (35)$$

a set of L_z highly nonlinear relations in the $2L_z$ unknowns, $U_A(z)$ and $U_B(z)$. Self-consistency provides the remaining L_z relations needed:

$$U_A(z) = \alpha(z) + \chi \langle \phi_B(z) \rangle, \quad (36)$$

with

$$U_B(z) = \alpha(z) + \chi \langle \phi_A(z) \rangle. \quad (37)$$

Only when the same $\alpha(z)$ can be chosen for both U_A and U_B is self-consistency satisfied. The so-called "hard-core" potential, $\alpha(z)$, is the usual internal potential, introduced in the random-phase approximation²⁶ to ensure incompressibility.

The calculation is initiated by making random initial guesses for the potential fields, U_A and U_B . The values of $U_A(z)$ and $U_B(z)$ are then continually adjusted until incompressibility and self-consistency are maintained, a numerical process of determining the roots of a nonlinear system of $2L_z$ equations in $2L_z$ unknowns.

IV. RESULTS AND DISCUSSION

Figure 3 shows the results of these numerical SCF calculations compared to the scaling prediction of Sec. II. Here, for molecular weights ranging from $N = 50$ to 500, and coverages ranging from $\sigma a^2 = 0.001$ to 0.1 is Z^* as determined numerically. Figure 4 shows schematically a typical end-monomer density profile as determined in the lattice SCF model, and the method used to determine Z^* . Essentially, the local maximum in $\xi''(z)$ occurring at the smallest z is used to determine Z^* from the numerical data. Generally, for $\chi \ll 18\sigma^2 a^4$, the linear scaling prediction is good, but there is a breakdown in scaling for $\chi \approx 18\sigma^2 a^4$. While the prediction that Z^* is equal to $\chi / (18\sigma^2 a^4)$ is clearly not borne out, it is clear that $\chi \sigma^{-2}$ is the appropriate scaling variable for this problem. Thus, for small coverage brushes in the classical

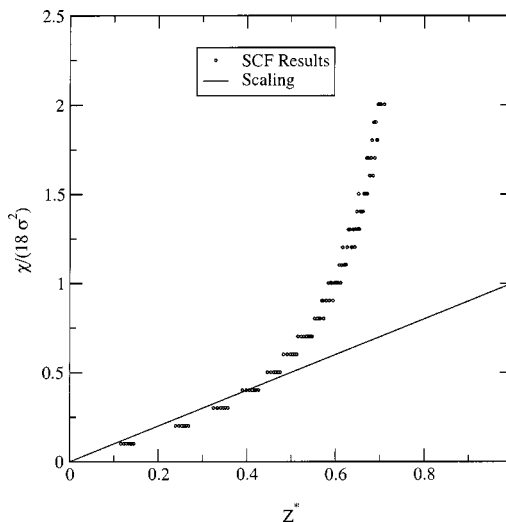


FIG. 3. Scaling for SCF: Z^* . Z^* as calculated in the numerical SCF calculations compared to the scaling prediction, Eq. (23).

limit (the most easily achieved scenario where the chains are Gaussian, yet fluctuations around the minimum free energy conformations are suppressed) the threshold for controlling the location of the free ends becomes a very sensitive function of χ and therefore temperature. It is clearly possible that a finely tunable control over the location and surface density of the chain free ends could be engineered from this system.

It should be pointed out that even for small χ the scaling prediction is more generally $z^*/h = b 18\sigma^2 a^4$, where the constant of proportionality $b \approx 0.9$. This is a consequence of the underestimation of the variation of $\phi_A(z)$ in the scaling argument, and represents a real effect. The general picture, however, is borne out quite well. As χ is increased, there is a continuous response Z^* , rather than the discontinuous response found in tethered diblock layers. Also, the width of the exclusion zone does not saturate at $Z^* = h/2$, as in the diblock case.

The composition gradient causes the existence of an end-exclusion zone, mimicking the behavior found for brushes

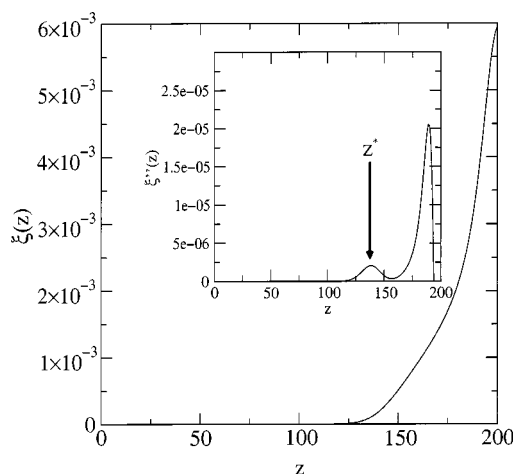


FIG. 4. Determining Z^* . The numerical determination of Z^* for $L = 200$, $N = 1667$, and $\chi = 0.5188$. The first peak in $\xi''(z)$ is used to locate the end-exclusion zone.

grafted to convexly curved substrates.^{19,27} Likewise, I expect that given the existence of an end-exclusion zone for flat surfaces with $\chi \approx \chi^*$, causing the substrate to take on a *concave* curvature may be sufficient to “fill-in” the exclusion zone. As has been pointed out, geometric features of the chain composition, and in particular hyperbranched architectures, also have the capability to drive free ends into the exclusion zone.²⁸ An interesting effect, left for future study, is how the interplay between hyperbranching and composition gradients along the arms of a dendritic polymer can control the end-distribution in dendrimers. Branching favors spreading the free tips out as evenly as possible, while the composition gradient drives the free ends toward the outer edge of the dendrimer. It is possible that the de Gennes and Hervet “hollow-core” dendrimer scenario can be achieved in such a system.²⁰ Scaling arguments and SCF analyses such as those carried out here will be able to make a definitive answer to this question, and provide an interesting prediction for experimental, synthetic, and materials engineering experimental initiatives.

V. CONCLUSION

I have shown through simple scaling arguments and a numerical self-consistent lattice approach that as a melt layer of end-grafted linear gradient polymers is cooled, free ends are progressively excluded from a growing zone enclosing the grafted surface. The important scale for the $A-B$ interaction when this effect is most important is $\chi \approx \chi^* = 18\sigma^2 a^4$. For small σ , it is likely that saturated layers, that is, physical manifestations of an Alexander–de Gennes polymer brush, can be achieved even for very small χ .

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