Abstract

We determine the distribution of free ends and the monomer insertion potential in the strongly-stretched limit for regularly and statistically branched polymer brushes. We find that the end density flattens in the limit of very strong branching with a concomitant enhancement of the grafting surface end density. This enhancement ensures for a wide range of parameters that a parabolic potential profile is preserved, even for large positive curvature of the brush surface. This considerably simplifies the analysis of copolymer phases.
1 Introduction

Geometrically branched molecules (small-molecule dendrimers [1] and dendritic polymers [2]) are seeing progressively sophisticated applications [3, 4], particularly as biomedical and drug-delivery agents [5]. The proliferation of free ends (possibly functionalized) and a rich design space in the interior of these single molecules makes them ideal as engineering platforms.

This work is particularly focused on determining the collective structure of large collections of dendritic or hyper-branched [6], polymers end-grafted on a surface [7]. Even ordinary, linear polymers gain interesting properties when they are crowded together onto a surface by one end. In making an analogy between the Edwards single-chain free energy and an electrostatic system, Semenov [8], and subsequently Milner, Witten, and Cates [9] (in making an analogy to the classical mechanics of a particle falling in an external potential), determined that the monomer chemical potential took on a universal profile - the “parabolic” potential (and density profile, when the polymer brush was solvated). Monodispersity of the chains is a very powerful constraint producing this behavior, as is the unique self-consistent potential thus determined. When the chains are grafted on a convex surface [10] the parabolic potential profile is no longer the self-consistent solution as such an ansatz would require monomers to overfill space near the grafting surface (so that the self-consistently determined distribution of free ends would be negative in some regions). A considerably more complex analysis is required to determine the self-consistent potential in the presence of regions with zero end-density (so-called “dead” or “exclusion” zones).

However, when the polymers in the brush are branched (star-like [11] or dendritic [12–14]) the architectural increase of free ends counteracts the “overfilling” effect, and it can occur that non-zero end-densities are achieved even for the extreme case of a single dendritic polymer in a good solvent. Here [14], the absence of dead-zones and the consequent parabolic potential and therefore monomer density causes a single dendritic polymer to have a dense core of monomers that decreases monotonically to its edge in good solvent. This is in contrast to the original
prediction \cite{16} that the tips of the dendritic polymer would all extend to the same spherical surface producing a large, characteristic “hollow core” which had eluded detection in early simulations \cite{17}. The monodispersity of the hyper-branched polymer is again the culprit, as a massive free-energy degeneracy is a consequence of the parabolic potential (and is the cause of the isochronous behavior of the harmonic oscillator \cite{15}).

In this work, we generalize a previous theory \cite{12, 13} as in Ref. \cite{14} in a “continuous branching” model for the dendrimer brush. Vastly different architectures (regularly branched, randomly branched, and various power-law schemes of branching) can all be handled in the same theory with few assumptions and fitting parameters. The parabolic shape of the insertion potential survives the continuous branching treatment, and is the exact analytic solution for an unreasonably large class of polymer brush architectures.

The paper is organized as follows. First, we introduce the strong stretching self-consistent theory for continuously branched brushes, then we analyze the end-distributions for various architectures. Finally we discuss the implications for the near-universal stabilization of the parabolic profile by branching, and make our conclusions.

2 Model

We use \( n \) as a “chemical index” marking the fewest monomers required from a given monomer to arrive at a non-grafted free end. Thus, each free tip has a chemical index of 0, and the unique grafted monomer has a chemical index of \( N \) (analogous to the overall molecular weight for a linear polymer). We denote the branching profile, \( f(n) \) to stand for the number of statistically equivalent monomers with the chemical index \( n \). For an unbranched polymer, \( f(n) = 1 \), while for a regular (double tip-splitting) dendritic polymer of generation \( G \), \( f(n) \) is an exponentially decreasing step function with \( f(0) = 2^G \) and discontinuities at \( n = 1/G, 2/G \ldots (G - 1)/G \). This branching profile has been used to analyze brushes of dendritic polymers \cite{12} and copolymers of dendritic polymers \cite{13} and brushes of star polymers \cite{11}. We can model polymers, however, with
continuous branching profiles, such as
\[
f(n) = 2^{-nG+G} \equiv e^{-bn}
\] (1)
as in [14] where the conformation of a single dendrimer was considered. The “branching index”, $b$ can be chosen so that we model polymers with $G$ generations and a junction functionality of 3 modeling tip-splitting dendrimers ... but any positive value of $b$ makes physical sense. This “continuously branched” polymer model has significant analytic advantages and loses only some of the (admittedly interesting) self-similar details of the exact free-end density. We will consider another class of branching profiles:
\[
f(n) = \left[ \frac{1 - \alpha n/N}{1 - \alpha} \right]^b
\] (2)
modeling polymers which are branched so that the average number of statistically equivalent monomers at any chemical index decreases as a power law from the free tips. Here, $\alpha$ is a measure of how strongly branched the polymers are, with the degree of branching diverging at $\alpha \to 1$. These two scenarios are depicted in Figure 1 (top panel).

At any rate, we consider a set of polymers characterized by a maximal chemical index $N$, of monomers of volume $a^3$ with the $n = N$ monomer irreversibly grafted to a flat surface with a grafting density of $\sigma$ chains per unit area. We consider a melt brush thus formed so that the overall height of the grafted layer is consistent with the incompressibility of the monomers:
\[
\frac{h}{\sigma} = a^3 \int_0^N dn f(n).
\] (3)
If $\sigma$ is large enough, then the chains in the brush will be considerably stretched from the grafting surface. As in Figure 1, the $n = N$ monomer is located at $z = 0$, and the $f(0)$ equivalent chain tips are located at $z = z_o < h$. The single-chain Edwards free energy of this chain is
\[
F_{\text{single}} = \int_0^N dn f(n) \left[ \frac{1}{2a^2} \left( \frac{dz}{dn} \right)^2 + a^3 P(z(n)) \right]
\] (4)
Under conditions in which $F_{\text{single}} >> 1$ (in natural energy units of $k_B T$), fluctuations of the chain conformations around the configuration which minimizes Eq. 4 are negligible, and all statistical averages can be calculated from the configurations minimizing the single chain free energy itself. Here, the first term counts the Gaussian elastic energy of $f(n)$ equivalent chains each consisting of $dn$ monomers and stretched a distance $dz$. The second term counts the energy required to evacuate a volume $a^3$ for each monomer in these test chains, at a cost in free energy of $P(z)a^3$. Thus, $P(z)$ is the monomer pressure in the layer, created by the crowding and the conformations of all of the other chains.

The minimization of Eq. 4 is effected through the usual calculus of variations, easily recognizable if the kernel of the integral is interpreted as the Lagrangian of a particle with a time-dependent mass in a gravitational field $-P(z)$:

$$L[z; \frac{dz}{dn}] = f(n) \left[ \frac{1}{2a^2} \left| \frac{dz}{dn} \right|^2 + a^3 P(z(n)) \right],$$

with the momentum conjugate to $z(n)$ given by

$$p = \frac{\partial}{\partial dz/dn} L = \frac{f(n)}{a^2} \frac{dz}{dn},$$

and the generalized force given by

$$f = \frac{\partial L}{\partial z} = f(n) a^2 \frac{d}{dz} P(z(n)).$$

Thus, the Euler-Lagrange equation governing the minimization of $F_{\text{single}}$ is

$$\frac{d}{dn} p = f$$

or

$$\frac{d}{dn} f(n) \frac{dz}{dn} = f(n) a^5 \frac{dP}{dz}.$$ 

The physical initial condition on this equation of motion is that

$$\frac{dz}{dn} \bigg|_{n=0} = 0,$$
thus requiring that there be no tension on the free chain end.

The pressure field, \( P \), can be calculated self-consistently from the solutions to Eq. 9. First, we need that \( P \) satisfies an isochronous property. Following the time-dependent mass analogy, a particle of mass \( f(t) \) released at rest from a position \( z_o \) must hit the grafting surface \( z = 0 \) when \( n = N \). This condition must obtain from every position with a non-zero density of free ends in the layer:

\[
N = \int_0^N dn = \int_0^{z_o} \frac{1}{\frac{dz}{dn}}.
\]  

(11)

Also, given such a \( P \) it must be possible to create a layer completely filled with monomers at every \( z \) without overfilling space for the melt brush we consider here. The common formulation of this condition is that the height density of free tips \( d\sigma/dz \) be positive:

\[
\Phi(z) \equiv 1 = \int_z^h dz_o \frac{d\sigma(z_o)}{dz_o} \phi(z; z_o)
\]  

(12)

with the volume fraction of monomers in the vicinity of \( z \) for a chain with its \( f(0) \) ends located at \( z_o \):

\[
\phi(z; z_o) = \sigma a^3 f(n) \frac{dn}{dz}.
\]  

(13)

When \( f(n) \equiv 1 \), (an ordinary polymer brush) self-consistency and the isochronous condition are satisfied when [9]

\[
P(z) = P_o (1 - \frac{z^2}{h^2})
\]  

(14)

with \( P_o = \pi^2/8a\sigma^2 \) and

\[
\frac{d\sigma}{dz} = \sigma \frac{z/h}{\sqrt{h^2-z^2}}.
\]  

(15)

remarkably compact and elegant expressions.

One approach to solving the self-consistency equations Eqs 11-12 when \( f(n) \neq 1 \) is to solve this set of integral equations for the unknown fields \( P(z) \) and \( d\sigma/dz \) simultaneously and numerically. However, knowing that an arbitrary \( f(n) \) gives the same physics as a time dependent mass in a gravitational field, we can be confident that the \textit{parabolic} pressure profile is a fruitful \textit{ansatz}. A
time-dependent mass in a harmonic gravitational potential will have the same falling time no matter where it is released from rest. The equation of motion under these conditions becomes:

\[
\frac{df}{dn} \frac{dz}{dn} + f(t) \frac{d^2z}{dn^2} = -2f(n)an^5P_oz
\]  

(16)

with \(dz/dn|_0 = 0\) where the pressure scale \(P_o\) still has to be determined self-consistently by enforcing \(z(N) = 0\) numerically.

To make further progress, we need to specify \(f(t)\), but there are two general results that can be gleaned at once. First, if the distribution of ends is non-zero for all \(0 < z < h\), the equation of motion is linear in \(z(n)\). Thus, the general solution with \(z(0) = z_o\) and \(z'(0) = 0\) satisfies:

\[
z(n) = z_o \xi(n),
\]

(17)

where \(\xi(n)\) is a solution to Eq (16) with

\[
\xi(0) = 1 \text{ and } \xi'(0) = 0.
\]

(18)

The final condition on \(\xi(n)\) is satisfied by choosing \(P_o\) such that

\[
\xi(N) = 0.
\]

(19)

Thus, the existence and uniqueness of \(\xi\) guarantees that the equal-time and minimum free energy conditions are satisfied. The non-negativity of the end-distribution must be checked separately.

The second is a general degeneracy theorem. The trajectory given by the solution to Eq (16) minimizes the overall single-chain free energy, Eq (4). We can very quickly show that all chain trajectories, regardless of the location of their free ends, \(z_o\), have the same single chain free energy. This massive degeneracy is the source of the “filled-core” dendrimer (as all sub-branch free energies with the subbranches starting at any position from the center out to the edge of the dendrimer have the same energy, and therefore add equally to the statistical averages determining the concentration profile). The minimum single-chain free energy is

\[
F_{\text{min}}[z(n)] = \int_0^N dn f(n) \left[ \frac{1}{2a^2} \left| \frac{dz}{dn} \right|^2 + a^3P_o(1 - \frac{z^2}{h^2}) \right].
\]

(20)
Rewriting the first term,
\[ \int_0^N dn f(n) \frac{1}{2a^2} \left( \frac{dz}{dn} \right)^2 = \int_0^N dn \left[ f(n) \frac{1}{2a^2} \frac{dz}{dn} \right] \frac{dz}{dn}, \]  
(21)
and integrating by parts:
\[ z(n)f(n) \frac{1}{2a^2} \left. \frac{dz}{dn} \right|_0^N - \int_0^N dn \left[ f(n) \frac{1}{2a^2} \frac{dz}{dn} \right] z = -\int_0^N a^3 P_o \frac{z^3}{h^2}, \]  
(22)
using the initial condition, the isochronous condition, and the equation of motion. Thus, the first term exactly cancels the \( z^2 \) term in the minimum free energy yielding:
\[ F_{\text{min}} = P_o a^3 \int_0^N f(n), \]  
(23)
so that an energy \( P_o a^3 \) must be paid to insert all of the \( \int dnf(n) \) monomers on the branched chain.

The free energy of a chain with its free ends located at \( z_o \) is thus independent of \( z_o \), so all of the chains contribute equally to the total layer energy. Thus, the parameter \( P_o \) is the overall monomer pressure to insert any monomer of volume \( a^3 \) into the brush.

It remains to calculate \( P_o \) given \( f(n) \) and to verify that the end-density is non-zero to verify the parabolic ansatz is a solution to the problem. When the brush is composed of geometrically branched polymers, and Eq.\[\text{\ref{integrate}}\] prevails, and the equation of motion becomes \( f(t) = e^{-bt} \):
\[ -b \frac{dz}{dt} + \frac{d^2z}{dt^2} = -2a^5 P_o z \]  
(24)
a “time-reversed” linear drag harmonic oscillator. When Eq.\[\text{\ref{bessel}}\] obtains (with the substitution \( u = (-1 + \alpha n/N) \)) the equation of motion is
\[ u z''(u) + z'(u) + \frac{2P_o a^5 N^2}{\alpha^2 h^2} uz = 0, \]  
(25)
a Bessel equation.

3 Results

We have determined both \( P_o \) and the end-density profiles by numerically solving Eq.\[\text{\ref{solve}}\] and by numerically inverting the integral equation Eq.\[\text{\ref{invert}}\]. Figure\[\text{\ref{fig1}}\] and Figure\[\text{\ref{fig2}}\] show how the insertion
potential per monomer depends on the relative degree of branching of the polymers in the brush. Here we refer to the “continuous branching” model of Ref. [14] as a continuous version of a tip-splitting dendritic polymer and the “power-law” brush corresponds to choice of \( f(n) \) corresponding to Eq. 2 with the the power-law parameter \( b = 1, 2, 3 \) in these calculations. When \( \alpha \to 1 \) the polymer has more and more equivalent ends.

We have scaled \( P_o \) to its value for a linear brush in the classical limit, \( \sigma^2 a \pi^2 / 8 \). In all of the cases we consider, it is apparent that the cost per monomer to establish the branched grafted layer decreases, and approaches zero in the limit of very high stretching. This is not to say that the overall free energy per chain decreases when the branching increases, as the energy per chain is proportional to the number of monomers. For chains of equivalent overall total chemical index \( N \) the cost at each \( n \) is \( f(n)P_o \), and thus is a rapidly increasing function with branching.

This does imply, however, that the stretching for most of the monomers with low \( n \) (and hence high \( f(n) \)) is very low. For hyper branched chains, this implies that the vicinity of the free ends acts essentially as densely cross-linked gel “buoy” tethered to the grafting surface by a set of very strongly stretched, but low overall molecular weight, tethers. The symptom of this in the free-end distributions would be a dramatic flattening and an enhancement of the end-density near the grafting surface, as in the lower panel of the schematic, Fig. 1. This is exactly what we note in Fig. 4 and Fig. 5. The \( G = 4 \) continuous branched layer and the \( \alpha = 3/4 \) linear power law brush have essentially uniform end-density across the layer. We note that the requirement for self-consistency is that \( \frac{d\sigma}{dn} > 0 \) throughout the brush, so that the parabolic ansatz is indeed the correct self-consistent inter-monomer interaction potential.

4 Discussion

Given how successful the parabolic ansatz is, it is tempting to jump to the erroneous conclusion that the parabolic potential is the self-consistent potential for any choice of \( f(n) \). The two choices we have made result in nicely analytic minimum-action trajectories, \( z(n; z_o) \), but the critical feature
required is that $f(n)$ be a decreasing function of chemical index. That is, the chains are unbranched at the grafting surface, and become more and more branched as they continue away from the grafting surface. If the chains started highly branched at the grafting surface, with subchains combining into loops as one left the grafting surface so that the chain became less and less branched toward the free ends then the brush will resemble a layer or Alexander-deGennes \[18\] \[19\] brushes of loops, with the free ends evacuated from a large region of the brush \[20\]. The self-consistent potential is then known to be radically different from the parabolic potential here, although the real potential still satisfies an isochronous, or monodisperse, condition.

Indeed, if we start with an unbranched set of chains, $f(n) = 1$, and alter the branching a bit by

$$f(n) = 1 + \varepsilon(n) \quad (26)$$

with $\varepsilon(n)$ a small function that is very strongly peaked at $n = 0$, it is easy to show that the surface end-density must be negative, and space is overfilled if the parabolic potential is followed. Essentially, we need to increase the number of chain free ends located with $z_o$ near the full brush height, $h$, above the unbranched limit. This causes the number of monomers entrained into the layer to be slightly larger than they would have been had $\varepsilon(n) = 0$, with the result that building the brush from the outer edge to the surface maintaining $\phi(z) = 1$ will overfill space with monomers at the grafting surface.

So, if $f(n)$ is a rapidly decreasing function of $n$, each chain “dumps” almost all of its monomers right in the vicinity of the free end location, $z_o$. In this case, the molten layer resembles a set of large, dense microgels tethered by much lower molecular weight net of branched chains. The minimum-action chain trajectories become (essentially) particles at rest for most of $n < N$, which then use their last few remaining monomers to fully stretch back to the grafting surface. Thus, the layer loses its character as an anisotropic stress environment, and becomes essentially a molten simple fluid of these free “heads” constrained to exist between $0 < z < h$, with a uniform density of “heads”. The rest of the brush is merely there to maintain the connectivity of the chains. The
flattening of the trajectories, and concomitant flattening of the chain end density distributions is the result.

The enrichment of the end-density at \( z = 0 \) has one more important consequence. If the grafting surface is convexly curved, the tendency of the branching to enhance the surface end-density and the curvature to decrease it will cancel in favor of non negative grafting surface density ... the critical “parabolic” curvature will of course depend upon the properties of the grafted and branched chains, but there is the possibility that copolymer phases of branched polymers (cylindrical, and spherical in particular) will be devoid completely of free-end “dead-zones,” making the estimate of the free energies of the phases elementary. Indeed, dead-zones of this type occur for energetic reasons as well, as in brushes of gradient copolymers [21]. It is an open question as to whether branching of the gradient copolymers will close that dead-zone.

5 Conclusion

In the self-consistent classical path analysis with a continuous branching profile, we have shown that the parabolic potential profile for hyper branched and statistically hyper branched polymers is the self-consistent chain interaction potential. This parabolic brush is remarkably robust to changing the chain topology and the melt-brush thus formed is (in the limit of strong branching) a simple liquid of “heads” tethered weakly to the surface by the last tether. Thus, branching dramatically simplifies the structure and analysis of these molten layers.
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**Figure Captions**

1. **Schematic.** The brush is constructed of polymers with chemical index running from $n = 0$ at the free end of the polymer to $n = N$ at the grafted end. The overall height of the layer is $h$, and $f(n)$ gives the number of statistically equivalent chains at a particular chemical index $n$. Dendritic polymers have a discontinuous $n$, and we model statistically branched polymers through continuous functions $f$. An exponential $f$ models a traditional dendritic polymer, while a power law $f$ models a set of polymers in which the probability of a branch point is not constant as a function of chemical index $n$.

2. **$P_o$ vs $\alpha$ for Power Law Branches.** The pressure per monomer (scaled to the unbranched result, $\sigma^2 a \pi^2 / 8$) as a function of the branching parameter $a$ for linear through cubic branching is shown. The parameter $\alpha$ controls the branching magnification: $f(n) = [(1 - \alpha (n/N))/(1 - \alpha)]^b$ for $b = 1, 2, 3$. The pressure vanishes when $\alpha \to 1$ consistent with a highly branched polymer brush being essentially a simple fluid of massive monomer “heads” connected to the grafting surface by single polymer strands. While the pressure per monomer decreases, the overall free energy per chain increases considerably as the branching increases, as there are more and more monomers per chain.

3. **$P_o$ vs. $G$ for Continuous Branching.** The pressure per monomer (scaled to the unbranched result, $P_o = \sigma^2 a \pi^2 / 8$ as a function of the effective generation of the dendritic polymer, $G$. Here, $f(n) = 2^{G(1-n/N)}$, so that there are $2^G$ branches at the free tips ($n = 0$) and a single branch at the grafting point ($n = N$). The pressure vanishes when $G \to \infty$ consistent with a highly branched polymer brush being essentially a simple fluid of massive monomer “heads” connected to the grafting surface by single polymer strands. While the pressure per monomer decreases, the overall free energy per chain increases considerably as the branching increases, as there are more and more monomers per chain.

4. **End Distributions for Continuously Branched Brushes.** Here we show the scaled end-density ($\frac{1}{\sigma} \frac{d\sigma(z)}{dz}$) as a function of scaled height in the brush $z/h$. We show various values of the effective dendrimer generation $G$. As $G$ increases, it is evident that the end-distribution becomes flatter and
flatter, and essentially uniform in the limit of high \( G \). Such a brush resembles a brush of “buoys”.

5 End Distributions for Power Law Branched Brushes Here we show the scaled end-density as a function of scaled height in the brush \( z/h \). For the linear power law \((b = 1)\) we show the end distribution for \( \alpha = 0, 0.25, 0.5, 0.75 \). The end-distribution is nonzero at all heights, and becomes flatter as \( \alpha \) increases.
Figure 1: Schematic.
Figure 2: $P_o$ vs. $\alpha$ for Power Law Branching.
Figure 3: $P_0$ vs. $G$ for Continuous Branching
End Density

Continuous Branched

Figure 4: End Distributions for Continuously Branched Brushes.
Figure 5: End Distributions for Power Law Branched Brushes.