Scaling behavior of a brush–homopolymer interface in the limit of high grafting density

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The interface between a polymer brush and a chemically equivalent homopolymer is examined using self-consistent field theory (SCFT). Focusing on ultrahigh grafting densities, we extract how the properties scale with the brush thickness, L, and compare with predictions based on strong-stretching theory (SST). Although the scaling exponents are consistent, the overall agreement is poor. We attribute this to the inaccurate way the SST-based calculation treats chain fluctuations at the extremity of the brush. This accounts for a previous disagreement between SCFT and SST in regards to autophobic dewetting, and brings into question a number of other SST predictions. Our conclusion is that SST requires a more sophisticated treatment of finite-stretching corrections, along the lines of that proposed by Likhtman and Semenov [Europhys. Lett. **51**, 307 (2000)]. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1883166]

I. INTRODUCTION

Polymeric brushes, formed by densely grafting polymer chains to a substrate as illustrated in Fig. 1, provide a simple way of modifying surface properties, such as adhesion, lubrication and wetting behavior. For high molecular weights, the polymers can be accurately treated by the Gaussian chain model,[1] for which the statistical mechanics can be solved using the self-consistent field theory (SCFT) introduced by Edwards[2] in 1965. Although SCFT is a conceptually elegant and simple theory, the mean field used to treat the molecular interactions has to be evaluated numerically. By assuming that the grafting density, σ, is sufficiently high that the chains become strongly stretched to such an extent that they are more or less restricted to ground-state or so-called *classical* configurations, Milner *et al.*[3] rationalized that the field can be approximated by

$$w(z) = -\frac{3\pi^2 z^2}{8a^2 N},\tag{1}$$

where z is the coordinate normal to the substrate, N is the number of segments in a brush chain, and a is the statistical segment length. In this parabolic potential, the *classical stretching* energy, $f(z_0)$, of a single chain extended to $z=z_0$ becomes

$$\frac{f(z_0)}{k_B T} = \frac{3\pi^2 z_0^2}{16a^2 N}.\tag{2}$$

For a neat brush (without solvent), the necessity for a uniform polymer concentration is achieved with a distribution of end-segments given by

$$g(z_0) = \frac{z_0 a N^{1/2}}{L\sqrt{L^2 - z_0^2}},\tag{3}$$

where z_0 cannot exceed the thickness of the brush, $L \equiv \sigma N / \rho_0$ (Here, ρ_0^{-1} is the volume of an individual segment). It follows from this strong-stretching theory (SST) that the free energy of a brush, F_b, is given by the simple analytical expression

$$\frac{F_b}{k_B T A \sigma} = \int_0^L g(z_0) \frac{f(z_0)}{k_B T} \frac{dz_0}{aN^{1/2}} = \frac{\pi^2 L^2}{8a^2 N},\tag{4}$$

where A is the total area of the substrate.

Although the convergence of SCFT to SST for densely grafted brushes is well established,[4] there are instances of serious disagreement between the two theories. Take, for example, the one involving autophobic dewetting, where a homopolymer film dewets from a chemically identical brush due to a positive brush–homopolymer tension of entropic origin.[5] While SCFT predicts[6] a tension, $\gamma_{b/h}$, consistent with experiment,[7] the SST prediction[8] is an order of magnitude larger than the actual measurements. This suggests that the underlying assumption in SST of strongly stretched chains (i.e., $L \gg aN^{1/2}$) is grossly inaccurate, but fortunately there is another less disturbing explanation. The tension arises from a difference in the free energy of a brush wet (i.e., covered) by homopolymer and that of a dry brush, and in this difference the leading-order approximation given by Eq. (4) completely cancels out. This makes the SST prediction for $\gamma_{b/h}$ exceptionally sensitive to the higher-order corrections of Eqs. (1)–(4), and thus the problem may simply reflect an inadequate or improper treatment of these finite-stretching corrections. Since most SST-based calculations only rely on the leading-order approximation, their predictions would remain valid. Nevertheless, there are a host of other phenomena[9–13] that, like autophobic dewetting, would be seriously affected.

This paper explores the origins of the autophobic-dewetting inconsistency by using SCFT to extract the accu-

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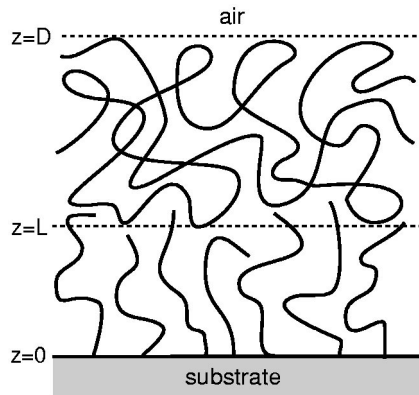[a)]Electronic mail: m.w.matsen@reading.ac.uk

FIG. 1. Schematic diagram of a polymer film of thickness, D, consisting of a strongly stretched polymer brush of height, L, covered (or wet) by a layer of chemically identical homopolymer. We refer to the brush as dry in the limit, $D \to L$.

rate scaling behavior of a polymer brush covered by a thick layer of high-molecular-weight homopolymer in the limit of high grafting density. We find that SCFT and SST predict vastly different finite-stretching corrections for the free energy of the brush. By elimination, we conclude that the problem lies with how SST accounts for chain fluctuations at the extremity of the brush, which implies the need for a more sophisticated treatment as provided by the advanced SST proposed by Likhtman and Semenov.[14]

II. THEORY

This section derives the SCFT and SST for a polymer film of area, A, and thickness, D, resting on a flat substrate (see Fig. 1). The film consists of n_b polymer chains of polymerization N uniformly grafted to the substrate, and n_h mobile homopolymer molecules of polymerization αN. The brush and homopolymer segments are assumed to be chemically identical, flexible with a statistical length a, and incompressible with a volume ρ_0^{-1}. The incompressibility implies that the volume of the film satisfies $V \equiv AD = (n_b + n_h \alpha)N/\rho_0$, which implies that the thickness of a dry brush is $L = \sigma N/\rho_0$, where $\sigma \equiv n_b/A$ is the grafting density. Hence, the brush thickness, L, is a direct measure of the grafting density, σ.

We orient our coordinate system with the z axis perpendicular to the film and position the substrate at $z=0$ with the air–polymer interface at $z=D$. For the planar geometry considered here, the chain statistics in the x-y plane decouple from those in the z direction and obey simple random-walk statistics.[1] However, in the z direction, the chains must deviate from a random walk to avoid overcrowding near the substrate. Rather than explicitly including the hard-core interactions responsible for this, a Lagrange-multiplier field is introduced to enforce a uniform polymer concentration by penalizing segments close to the substrate. In principle, the field must fluctuate in order to maintain a truly uniform concentration [i.e., $\hat{\phi}(\mathbf{r})=1$]. However, to make the problem tractable, we assume a static field, $w(z)$, that just constrains the average concentration [i.e., $\phi(\mathbf{r}) \equiv \langle \hat{\phi}(\mathbf{r}) \rangle = 1$], which amounts to the well-known mean-field approximation.

A. Self-consistent field theory

SCFT performs the statistical mechanics of our model without any further approximations beyond that of mean-field theory. It starts by evaluating a partition function, $q_f(z,s)$, for a chain fragment of sN segments with one end fixed at z and the other end free, as well as a similar partition function, $q_g(z,s)$, where instead the second end is grafted to the substrate at $z=0$. Both functions satisfy the same diffusion equation

$$\frac{\partial}{\partial s}q(z,s) = \left[\frac{a^2 N}{6} \frac{\partial^2}{\partial z^2} - w(z) \right] q(z,s), \qquad (5)$$

subject to reflecting boundary conditions at $z=0$ and $z=D$.[1] The only difference between them is that the first begins with the initial condition $q_f(z,0)=1$, while the second starts off as $q_g(z,0)=2\delta(z)aN^{1/2}$.

Once the partition functions are known, the concentration of brush chains is given by

$$\phi_b(z) = \frac{L}{\mathcal{Q}_b} \int_0^1 q_g(z,1-s)q_f(z,s)ds, \qquad (6)$$

where

$$\mathcal{Q}_b = \int_0^D q_g(z,1-s)q_f(z,s)dz = q_f(0,1)aN^{1/2} \qquad (7)$$

is the partition function for a complete brush chain. The integral in Eq. (7) can be evaluated for any value of s but it is most convenient to use $s=1$. Similarly, the homopolymer concentration is

$$\phi_h(z) = \frac{D-L}{\alpha \mathcal{Q}_h} \int_0^\alpha q_f(z,\alpha-s)q_f(z,s)ds, \qquad (8)$$

where

$$\mathcal{Q}_h = \int_0^D q_f(z,\alpha-s)q_f(z,s)dz = \int_0^D q_f(z,\alpha)dz \qquad (9)$$

is the partition function for a complete homopolymer chain. The combination of brush and homopolymer segments must satisfy the incompressibility condition

$$\phi_b(z) + \phi_h(z) = 1, \qquad (10)$$

which is the criterion used to adjust $w(z)$.

Once the field is determined self-consistently, the free energy of the brush, F_b, is specified by

$$\frac{F_b}{k_B T} = -n_b \ln\left(\frac{\mathcal{Q}_b}{aN^{1/2}} \right) - \frac{\rho_0 A}{N} \int_0^D w(z)\phi_b(z)dz, \qquad (11)$$

and the free energy of the homopolymer, F_h, is

$$\frac{F_h}{k_B T} = -n_h \ln\left(\frac{e\mathcal{Q}_h}{n_h aN^{1/2}} \right) - \frac{\rho_0 A}{N} \int_0^D w(z)\phi_h(z)dz. \qquad (12)$$

Note that $\ln(n_h!) \approx n_h \ln(n_h/e)$ has been added to account for the indistinguishability of the homopolymer molecules; this is responsible for the extra factors in the logarithmic term. For convenience, the free energy expressions, Eqs. (11) and (12), will be divided by $A\sigma = n_b = \rho_0 AL/N$ to provide inten-

sive quantities independent of the system size.

In the interest of minimizing the number of approximations in the upcoming SST treatment, we now exploit a convenient simplification that occurs for large homopolymer molecules (i.e., $\alpha \to \infty$). In this limit, the partition function becomes[1,15]

$$q_f(z,s) \propto \psi(z)\exp(-\lambda s), \tag{13}$$

where λ and $\psi(z)$ are the ground-state eigenvalue and eigenfunction, respectively, of

$$\left[\frac{a^2 N}{6}\frac{\partial^2}{\partial z^2} - w(z)\right]\psi(z) = -\lambda\psi(z). \tag{14}$$

From this, it follows that the homopolymer profile reduces to

$$\phi_h(z) \propto \psi^2(z), \tag{15}$$

where the proportionality constant can be determined by the requirement

$$\int_0^D \phi_h(z)dz = D - L. \tag{16}$$

Furthermore, the homopolymer free energy reduces to

$$\frac{F_h}{k_B T A \sigma} = \lambda\left(\frac{D}{L} - 1\right) - \frac{1}{L}\int_0^D w(z)\phi_h(z)dz. \tag{17}$$

This is the expression used to calculate F_h in the SCFT, but with a little manipulation,[1] the homopolymer free energy can be rewritten as

$$\frac{F_h}{k_B T A \sigma} = \frac{a^2 N}{24 L}\int_0^D \frac{[\phi_h'(z)]^2}{\phi_h(z)}dz, \tag{18}$$

which is a form that can be readily incorporated into the SST without introducing any approximations. In this way, we can be sure that any discrepancy between SCFT and SST is entirely due to inaccuracies in the SST treatment of the brush chains.

To examine SCFT for $L \gg aN^{1/2}$, we use the real-space algorithm discussed in Ref. 4. This implements the Crank–Nicholson algorithm to solve the diffusion Eq. (5) and the trapezoid method to evaluate the integrals, which is a combination that rigorously conserves the net concentration of brush segments. To achieve the necessary accuracy at large L, the grid-size has to be particularly fine (i.e., $\Delta z/aN^{1/2} = 8 \times 10^{-4}$ and $\Delta s = 5 \times 10^{-5}$). For the homopolymer, a standard predictor–corrector method is used to integrate Eq. (14) for $\psi(z)$ starting from $z=D$, while λ is adjusted using a simple bisection method so that $\psi(z) \to 0$ as $z \to 0$. Finally, the incompressibility condition, $\phi_b(z) + \phi_h(z) = 1$, is solved to high accuracy (i.e., 1 part in 10^9) by adjusting $w(z)$ according to the Broyden algorithm. Note that D has to be chosen large enough that $\phi_b(D) \approx 0$.

B. Strong-stretching theory

SST is an approximation to SCFT that, in principle, becomes exact in the limit, $L \to \infty$. The current version of SST used to describe a brush–homopolymer interface was first proposed by Semenov.[9] It uses the exact expression, Eq. (18), for the homopolymer free energy, and approximates the free energy of the brush by

$$\frac{F_b}{k_B T A \sigma} = \frac{1}{L}\int_0^\infty \left[\frac{3\pi^2 z^2 \phi_b(z)}{8a^2 N} + \frac{a^2 N[\phi_b'(z)]^2}{24\phi_b(z)}\right]dz. \tag{19}$$

The first term gives the classical stretching energy, where the chains follow classical trajectories in the parabolic potential of Eq. (1).[16] Notice that for a step profile, this term reproduces the free energy given by Eq. (4). Even when L is large, the free ends of the brush chains are weakly stretched and thus can easily deviate from their classical trajectories. The second term, which is analogous to Eq. (18), supposedly accounts for these chain fluctuations. Note that a rigorous justification for the use of Eq. (18) in this particular context has yet to be provided.

The equilibrium free energy of the combined system is obtained by minimizing $F_b + F_h$ subject to the incompressibility constraint in Eq. (10). In the interest of obtaining an analytical prediction, Semenov assumed a profile of the functional form

$$\phi_b(z) = \frac{1}{2}\left[1 - \tanh\left(\frac{2(z-L)}{w_{b/h}}\right)\right], \tag{20}$$

where $w_{b/h}$ is the width of the brush–homopolymer interface. Given this assumption

$$\frac{F_b + F_h}{k_B T A \sigma} = \frac{\pi^2 L^2}{8a^2 N} + \frac{\pi^4}{128}\left(\frac{w_{b/h}}{aN^{1/2}}\right)^2 + \frac{aN^{1/2}}{6L}\left(\frac{w_{b/h}}{aN^{1/2}}\right)^{-1}. \tag{21}$$

Minimization with respect to the interfacial width gives

$$\frac{w_{b/h}}{aN^{1/2}} = \frac{4}{\pi(6\pi)^{1/3}}\left(\frac{L}{aN^{1/2}}\right)^{-1/3}. \tag{22}$$

With that, the free energy of the brush reduces to

$$\frac{F_b}{k_B T A \sigma} = \frac{\pi^2 L^2}{8a^2 N} + \frac{\pi(6\pi)^{1/3}}{24}\left(\frac{L}{aN^{1/2}}\right)^{-2/3}, \tag{23}$$

and the free energy of the homopolymer becomes

$$\frac{F_h}{k_B T A \sigma} = \frac{\pi(6\pi)^{1/3}}{48}\left(\frac{L}{aN^{1/2}}\right)^{-2/3}. \tag{24}$$

While the above approximation produces convenient expressions, it does not represent the true free energy minimum. In order to avoid any debate over whether or not this approximation makes a significant contribution to the discrepancy with SCFT, we now minimize $F_b + F_h$ numerically without any *a priori* assumptions of the profile. This must be done subject to the constraint

$$\frac{\Phi_b}{k_B T A_\sigma} \equiv \frac{1}{L}\int_0^\infty \phi_b(z)dz = 1, \tag{25}$$

and therefore we minimize $\Omega \equiv F_b + F_h - \Lambda\Phi_b$, where Λ is a Lagrange multiplier. However, for convenience, we define an alternative multiplier, z_I, by $\Lambda \equiv 3\pi^2 z_I^2/8a^2 N$, so that

$$\frac{\Omega}{k_B T A \sigma} = \frac{1}{L} \int_0^\infty \left[\frac{3\pi^2(z^2 - z_I^2)\phi_b(z)}{8a^2 N} \right.$$

$$\left. + \frac{a^2 N [\phi_b'(z)]^2}{24\phi_b(z)(1 - \phi_b(z))} \right] dz. \tag{26}$$

To simplify this expression further, we then define $\phi_b(z) \equiv \sin^2 \Theta(z)$, such that

$$\frac{\Omega}{k_B T A \sigma} = \frac{1}{L} \int_0^\infty \left[\frac{3\pi^2(z^2 - z_I^2)}{8a^2 N} \sin^2 \Theta(z) \right.$$

$$\left. + \frac{a^2 N}{6} [\Theta'(z)]^2 \right] dz, \tag{27}$$

for which the Euler–Lagrange equation is

$$\Theta''(z) = \frac{9\pi^2(z^2 - z_I^2)}{2a^2 N} \sin \Theta(z) \cos \Theta(z). \tag{28}$$

Assuming the thick-brush limit, we look for a solution where $\Theta(z) = \pi/2$ for $z \ll L$ and $\Theta(z) = 0$ for $z \gg L$. From the above equation, it follows that $z = z_I$ corresponds to the inflection point in $\Theta(z)$, which must occur relatively close to $z \approx L$. Therefore, as the brush becomes thick $(z^2 - z_I^2) \to 2L(z - z_I)$ in the vicinity of the interface. This reduces the Euler–Lagrange equation to

$$\Theta''(u) = \frac{9\pi^2(u - u_I)}{2} \sin \Theta(u) \cos \Theta(u), \tag{29}$$

where $u \equiv (z - L)L^{1/3}/a^{4/3}N^{2/3}$ is an appropriate scaling variable. The constraint used to determine u_I becomes

$$\int_0^\infty \sin^2 \Theta(u) du = \int_{-\infty}^0 \cos^2 \Theta(u) du. \tag{30}$$

Given the symmetry of the equations, the inflection point must occur at $u_I = 0$ with $\Theta(-u) = \pi/2 - \Theta(u)$, which in turn implies $\Theta(0) = \pi/4$. Then it is simply a matter of adjusting $\Theta'(0) = 1.9417$ so that $\Theta(u) \to 0$ as $u \to \infty$, which is done numerically. The resulting free energy of the brush is

$$\frac{F_b}{k_B T A \sigma} = \frac{\pi^2 L^2}{8a^2 N} + 0.3464 \left(\frac{L}{aN^{1/2}} \right)^{-2/3}, \tag{31}$$

and the free energy of the homopolymer becomes

$$\frac{F_h}{k_B T A \sigma} = 0.1732 \left(\frac{L}{aN^{1/2}} \right)^{-2/3}. \tag{32}$$

The true profile does, in fact, differ noticeably from the assumption in Eq. (20); in particular, its interfacial width, $w_{b/h} \equiv |\phi_b'(L)|^{-1}$, is about 8% greater than that predicted by Eq. (22). However, the free energies in Eqs. (31) and (32) are virtually indistinguishable from those in Eqs. (23) and (24), respectively, and so the former analytical calculation is well justified.

III. RESULTS

Now we compare the SCFT and SST predictions for various aspects of a polymer brush wet by a macroscopic layer of infinite-molecular-weight homopolymer (see Fig. 1).
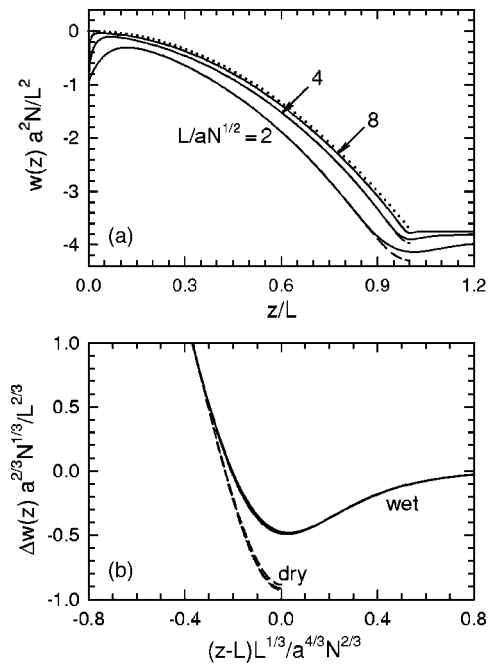

FIG. 2. (a) Self-consistent fields, $w(z)$, for wet (solid curves) and dry (dashed curves) brushes of various thickness, L. The dotted curve denotes the SST prediction in Eq. (1). (b) Scaling plot of $\Delta w(z) \equiv w(z) - \lambda$ demonstrating the behavior of the fields in the limit $L \to \infty$.

Also included are comparisons with our previous SCFT calculations[4] for a dry brush with the homopolymer layer removed (i.e., $D \to L$). In the dry-brush limit, the field is reflected about $z = L$ and the chains are permitted to extend into the region $z > L$, with the caveat that the incompressibility condition be satisfied when those segments are reflected back to $z < L$ [i.e., $\phi_b(L + \epsilon) + \phi_b(L - \epsilon) = 1$]. This way of satisfying the reflecting boundary condition at the outer edge of the brush amounts to considering two identical opposing brushes. Note that there is an unfortunate clash of terminologies in the use of "wet" and "dry." Our present use conforms to the general subject of interfacial wetting, where wet implies that the brush is separated from the air by a macroscopic layer of homopolymer. This should not be confused with the alternative meaning specific to polymer brushes, where wet would imply significant penetration of the homopolymer into the brush.

The first quantity we consider is the self-consistent field, $w(z)$, plotted in Fig. 2 for a range of grafting densities. Plot (a) scales the field and the z coordinate with respect to L, such that the SST prediction in Eq. (1) corresponds to the single dotted curve. The SCFT predictions for wet and dry brushes are shown with solid and dashed curves, respectively. Because additive constants to $w(z)$ have no consequence on the statistical mechanics of the chains, the curves in Fig. 2(a) can be shifted vertically by any arbitrary amount. We do so such that the SCFT predictions match up with the full classical theory (FCT), which is a more accurate version of SST examined in Ref. 17. As expected, the SCFT results for both the wet and dry brushes approach the SST prediction as $L \to \infty$. Also notice that the wet- and dry-brush fields are virtually indistinguishable for $z \ll L$.

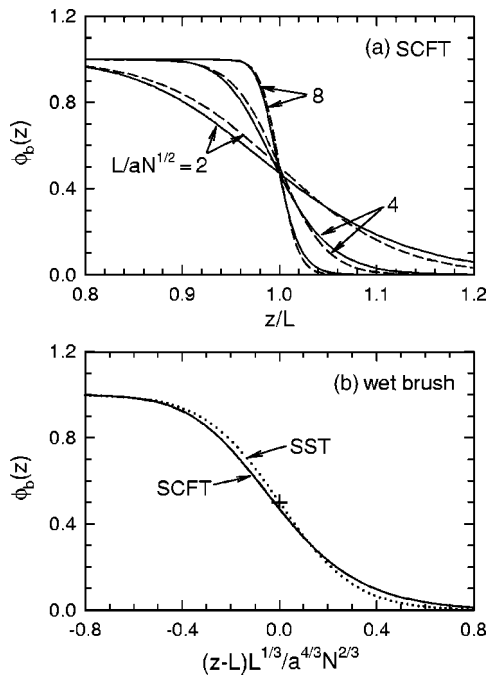Moving our attention to the interface (i.e., $z \approx L$), we

FIG. 3. (a) Brush profile, $\phi_b(z)$, for wet (solid curves) and dry (dashed curves) brushes of various thickness, L. (b) Scaling plot of the wet-brush results compared against the SST prediction (dotted curve) calculated by Eq. (29). Note that the SST curve is symmetric with respect to a 180° rotation about the cross at $z=L$ and $\phi_b(L)=0.5$

FIG. 4. (a) End-segment distribution, $g(z_0)$, for wet (solid curves) and dry (dashed curves) brushes of various thickness, L. (b) Scaling plot of the wet-brush results compared against the SST prediction (dotted curve) in Eq. (36).

focus on where the wet- and dry-brush fields begin to differ. According to Eqs. (14) and (15), the wet-brush field must be related to the homopolymer concentration by

$$ w(z) = \lambda + \frac{a^2 N}{6\sqrt{\phi_h(z)}} \frac{\partial^2}{\partial z^2} \sqrt{\phi_h(z)}. \qquad (33) $$

Furthermore, SST predicts that the homopolymer profiles, $\phi_h(z) = 1 - \phi_b(z)$ for different L collapse onto a single curve when plotted as a function of $u \equiv (z-L)L^{1/3}/a^{4/3}N^{2/3}$. From this, we deduce the appropriate scaling in Fig. 2(b) by which the differences, $\Delta w(z) \equiv w(z) - \lambda$, collapse onto a single curve. When we subtract the same λ off of the dry-brush fields, they also collapse onto a single master curve. Note that because SST strictly assumes Eq. (1) in the brush-rich region and Eq. (33) in the homopolymer-rich region, it does not provide a consistent prediction for $w(z)$ in the interfacial region.

Next we plot the SCFT profiles, $\phi_b(z)$, of both wet and dry brushes in Fig. 3(a) for a series of different grafting densities. Our first observation is that the chains are slightly more stretched when the brush is wet by a layer of homopolymer. Figure 3(b) demonstrates that the width of the brush–homopolymer interface scales as $L^{-1/3}$, as predicted by SST in Eq. (22). The dotted curve is the accurate SST profile obtained by the full numerical minimization of the free energy. Although the SCFT and SST results are reasonably similar, there exists an important qualitative difference. The SST prediction has a symmetry about $z=L$ [specifically, $\phi_b(L+\epsilon) = 1 - \phi_b(L-\epsilon)$], which is distinctly absent from the SCFT profiles. The significance of this discrepancy will be discussed in the next section.
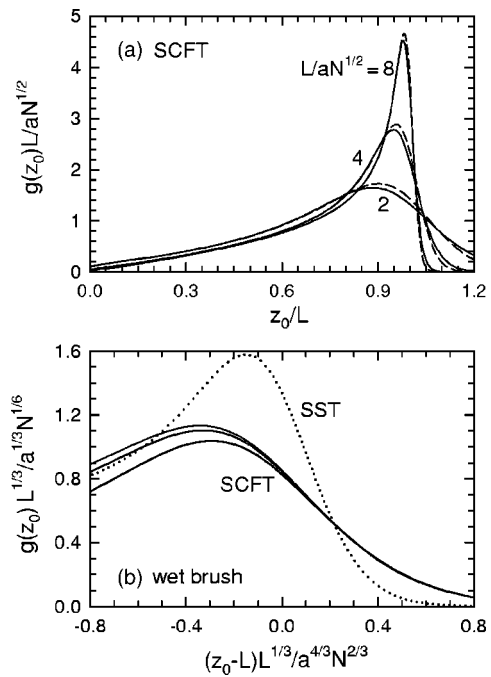
A more direct measure of the chain stretching is provided by the end-segment distribution function, $g(z_0)$. In SCFT, the distribution is given by

$$ g(z_0) = \frac{aN^{1/2}}{Q_b} q_g(z_0, 1), \qquad (34) $$

normalized such that $\int g(z_0) dz_0 = aN^{1/2}$. Figure 4(a) compares the wet- and dry-brush distributions for a series of different brush thicknesses. In the interior of the brush, the distributions are virtually identical, but for those chains extending to the interfacial region, the degree of stretching is greater for the wet brush consistent with our conclusion based on the profiles, $\phi_b(z)$.

According to SST,[13] the end-segment distribution is related to the brush profile by

$$ g(z_0) = -\frac{z_0 aN^{1/2}}{L} \int_{z_0}^{\infty} \frac{\phi_b'(z)}{\sqrt{z^2 - z_0^2}} dz. \qquad (35) $$

In the limit of a step profile, we recover Eq. (3). Provided that the interface remains reasonably steep, the main contribution to the integral comes from $z \approx L$. It follows that in the interfacial region (i.e., $z_0 \approx L$), we can approximate $\sqrt{z^2 - z_0^2} \approx \sqrt{2L(z-z_0)}$, in which case

$$ g(z_0) \approx -\frac{1}{\sqrt{2}} \left(\frac{L}{aN^{1/2}} \right)^{-1/3} \int_{u_0}^{\infty} \frac{\phi_b'(u)}{\sqrt{u-u_0}} du, \qquad (36) $$

where $u_0 \equiv (z_0 - L)L^{1/3}/a^{4/3}N^{2/3}$. This predicts a universal distribution when $g(z_0)L^{1/3}$ is plotted against u_0 as shown by the dotted curve in Fig. 4(b). Indeed, the SCFT predictions from Fig. 4(a) collapse when scaled in this manner, but with much different master curves than predicted by SST.
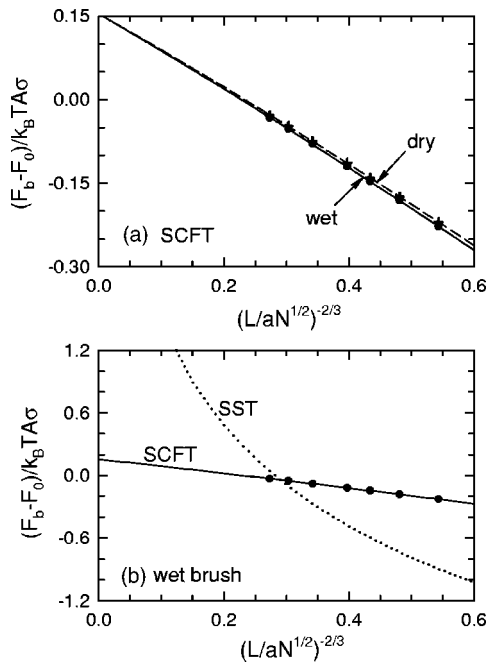
FIG. 5. (a) Free energy of the brush, F_b, relative to F_0 from Eq. (37) plotted as a function of the brush thickness, L. The solid dots denote the SCFT calculations, while the solid curve represents the fit given by Eq. (38). The crosses and dashed curve compare analogous results for the dry brush examined in Ref. 4. (b) Equivalent plot, but at a sufficiently reduced scale so as to show the SST prediction (dotted curve) from Eq. (31). For purposes of comparison, the SST curve has been shifted vertically.

It has been established[4,14] that for sufficiently large L, the free energy of a brush is given by $F_b \approx F_0$, where

$$\frac{F_0}{k_BTA\sigma} \equiv \frac{\pi^2 L^2}{8a^2N} - \ln\left(\frac{3^{1/2}L}{2aN^{1/2}}\right). \quad (37)$$

This includes the classical stretching energy from Eq. (4) along with a logarithmic correction originating from the translational entropy, $-k_B\int g(z_0)\ln g(z_0)dz_0$, of the chain ends.[14] Figure 5(a) shows the residual free energy, F_b-F_0, plotted in terms of $L^{-2/3}$, where the exponent is motivated by Ref. 14. The solid dots represent points calculated by SCFT, and the curve through them is given by

$$\frac{F_b - F_0}{k_BTA\sigma} \approx 0.1544 - 0.659\left(\frac{L}{aN^{1/2}}\right)^{-2/3}$$

$$- 0.083\left(\frac{L}{aN^{1/2}}\right)^{-4/3}. \quad (38)$$

The constant, 0.1544, is derived in Ref. 14 (see Ref. 18 for additional details) and occurs due to a narrow *proximal layer* next to the substrate, where the field in Fig. 2(a) deviates significantly from the parabolic potential. The other two coefficients, −0.659 and −0.083, are obtained by a least-squares fit to the SCFT data. The dashed curve compares an equivalent fit from Ref. 4 for dry brushes, for which the fitting coefficients were −0.640 and −0.092, respectively. It turns out that the SST prediction of F_b in Eq. (31) is so seriously inaccurate that the reduced scale of Fig. 5(b) is needed in order to compare it with SCFT.

The last quantity we consider is the homopolymer free energy, F_h, in Fig. 6 plotted versus $L^{-2/3}$, as motivated by the
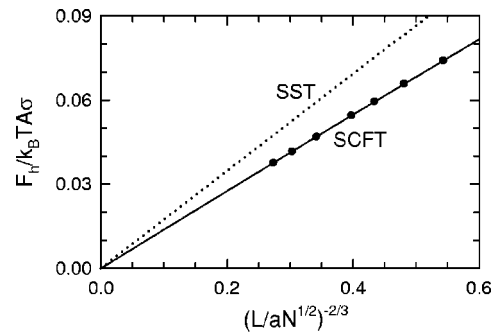

FIG. 6. Homopolymer free energy, F_h, as a function of brush thickness, L. The solid dots denote the SCFT calculations and the solid curve shows the fit specified by Eq. (39). The SST prediction from Eq. (32) is denoted by the dotted curve.

SST prediction in Eq. (32). Again the solid dots denote the SCFT calculations, while the curve represents a least-squares fit

$$\frac{F_h}{k_BTA\sigma} \approx 0.139\left(\frac{L}{aN^{1/2}}\right)^{-2/3} - 0.005\left(\frac{L}{aN^{1/2}}\right)^{-4/3}. \quad (39)$$

In this case, the coefficient 0.139 is reasonably similar to the SST prediction of 0.173. This should be expected since SST utilizes the exact free energy expression in Eq. (18), and so the only possible source of inaccuracy comes from that of the profile displayed in Fig. 2(b). The SST coefficient is larger simply because it predicts a narrower brush–homopolymer interface.

IV. DISCUSSION

By combining the present study with our previous one[4] for dry brushes, we can evaluate the tension, $\gamma_{b/h}=(F_b+F_h-F_b^{(\mathrm{dry})})/A$, responsible for autophobic dewetting. Here the superscript "(dry)" denotes the free energy of a dry brush with no homopolymer on its surface. In general, a dewetted brush will contain trace amounts of residual homopolymer,[6] but this vanishes in the limit of $\alpha\to\infty$. Therefore, we have

$$\frac{\gamma_{b/h}N^{1/2}}{k_BTa\rho_0} = 0.120\left(\frac{L}{aN^{1/2}}\right)^{1/3} + 0.004\left(\frac{L}{aN^{1/2}}\right)^{-1/3}. \quad (40)$$

In the difference, $F_b-F_b^{(\mathrm{dry})}$, there is a complete cancellation of F_0 from Eq. (37) as well as the constant, 0.1544, originating from the proximal layer. Consequently, the brush and homopolymer contributions $(F_b-F_b^{(\mathrm{dry})})/A$ and F_h/A, respectively, are both of order $L^{1/3}$, using the fact that $\sigma \propto L$. Nevertheless, the coefficient of 0.120 in Eq. (40) is almost entirely due to the 0.139 from the homopolymer free energy in Eq. (39). Also notice that the tiny contribution from the brush free energy acts to reduce $\gamma_{b/h}$ slightly.

The SST treatment by Leibler *et al.*[8] predicts a brush/homopolymer tension of

$$\frac{\gamma_{b/h}N^{1/2}}{k_BTa\rho_0} = \frac{\pi(6\pi)^{1/3}}{16}\left(\frac{L}{aN^{1/2}}\right)^{1/3} \approx 0.523\left(\frac{L}{aN^{1/2}}\right)^{1/3}, \quad (41)$$

which is far larger than that of SCFT. Furthermore, the homopolymer contribution to the coefficient 0.523 is only a meager 0.174. This tremendous inaccuracy can be traced to

the fact that SST approximates the dry-brush free energy by Eq. (4) without any corrections for finite L. This can be immediately improved upon by appealing to the equivalent system of two opposing brushes, where $\phi_b(z)$ extends beyond $z=L$ subject to the constraint, $\phi_b(z)+\phi_b(2L-z)=1$. In this case, Eq. (19) predicts

$$\frac{F_b^{(\mathrm{dry})}}{k_B T A \sigma} \approx \frac{\pi^2 L^2}{8a^2 N} + \frac{\pi(12\pi)^{1/3}}{32}\left(\frac{L}{aN^{1/2}}\right)^{-2/3}, \qquad (42)$$

assuming the analytical profile in Eq. (20). With this improvement, the SST prediction becomes

$$\frac{\gamma_{b/h} N^{1/2}}{k_B T a \rho_0} = \frac{\pi(6\pi)^{1/3}}{16}(1-2^{-2/3})\left(\frac{L}{aN^{1/2}}\right)^{1/3}$$

$$\approx 0.193\left(\frac{L}{aN^{1/2}}\right)^{1/3}, \qquad (43)$$

where the coefficient, 0.193, is now much closer to the SCFT value of 0.120, and where it is now dominated by the homopolymer free energy.

Although we now have a SST prediction for $\gamma_{b/h}$ that is in reasonable agreement with SCFT, a closer look reveals that there are still serious problems. Beyond the zeroth-order approximation in Eq. (4), the SST predictions for F_b and $F_b^{(\mathrm{dry})}$ are terribly inaccurate. Granted they omit the logarithmic term in Eq. (37) because the translational entropy of the chain ends has not been considered, but also the coefficients for the $L^{-2/3}$ terms are positive when in fact they should be negative. Furthermore, SCFT shows that $F_b-F_b^{(\mathrm{dry})}$ is negative, while even the improved SST treatment predicts this to be positive. It is simply fortuitous that for the particular quantity, $\gamma_{b/h}$, there is an approximate cancellation of errors.

The present SST treatment for $\gamma_{b/h}$ has three contributions, of which two are well justified. First of all, it utilizes the exact SCFT expression in Eq. (18) for the configurational entropy of the homopolymer, which is rigorously derived in Ref. 1. Second of all, the classical stretching energy of the brush in Eq. (19) also has a rigorous derivation.[16] By elimination, our suspicion falls to the second brush term involving the gradient of $\phi_b(z)$, which supposedly accounts for chain fluctuations. This term may appear reasonable based on its equivalence with the homopolymer free energy, but a formal derivation has never been provided nor is it clear how the proof for the homopolymer case could be extended to that of the brush. The relation in Eq. (33) between $w(z)$ and $\phi_h(z)$ seems to rule this out, since it cannot simultaneously apply to the brush. After all, the two profiles, $\phi_b(z)$ and $\phi_h(z)$, would predict different fields, but the brush and homopolymer must experience the same field since they are chemically identical.

There are a couple further discrepancies between SCFT and SST that add to our suspicion regarding the second term in Eq. (19). First of all, there is an important difference in the predicted shape of the end-segment distribution, $g(z_0)$, plotted in Fig. 3(b). Although the agreement for the brush profile, $\phi_b(z)$, in Fig. 2(b) is much better, there is still a significant qualitative difference. The SST profile has a symmetry about $z=L$ [specifically, $\phi_b(L+\epsilon)=1-\phi_b(L-\epsilon)$], which can be traced to the fact that SST employs identical gradient terms for the homopolymer and brush, Eqs. (18) and (19), respec-

tively. This symmetry is clearly violated by the SCFT profile, indicating that the exterior of the brush should be treated differently than the homopolymer.

Even if there does exist a legitimate derivation for the second term in Eq. (19), the approximations involved must nevertheless be highly inaccurate. Fortunately, there exists an alternative SST treatment for the finite-stretching corrections to Eq. (4) that has been proposed by Likhtman and Semenov[14] and successfully tested against SCFT.[4] It predicts the first three terms in F_b exactly (i.e., F_0 and the constant, 0.1544) and provides a reasonable estimate for the $L^{-2/3}$ coefficient (with the correct sign). If SST is to be applied to such problems as autophobic dewetting, this more advanced SST needs to be implemented.

There are other calculations, in addition to those of autophobic dewetting[6,8,13] that are dominated by the finite-stretching corrections to SST, and thus are similarly affected by our conclusions. These include the original applications[9–11] of Eq. (19) to block copolymer–homopolymer blends, as well as more recent calculations for the effective interaction between brush-coated colloidal particles.[12] In light of our present findings, the resulting predictions should be viewed with a degree of caution.

V. CONCLUSIONS

The accurate scaling behavior of strongly stretched brushes in contact with their parent homopolymer has been determined using self-consistent field theory (SCFT). Combining this with previous SCFT results[4] for dry brushes, we also derive a scaling expression for the brush–homopolymer tension, $\gamma_{b/h}$, responsible for autophobic dewetting. Although the expression, Eq. (40), is intended for $L \gg aN^{1/2}$, it remains reasonably accurate for the experimentally relevant conditions (i.e., $L \sim aN^{1/2}$) examined in Ref. 6. On the other hand, the previous analytical prediction in Ref. 8 based on strong-stretching theory (SST) proves to be grossly inaccurate. Although the SST prediction can be improved with a better treatment of the dry brush, there still remains serious problems with the theory.

By elimination, we attribute these problems to the way SST treats finite-stretching corrections by the second term in Eq. (19), which is apparently motivated by an analogy with the homopolymer free energy in Eq. (18). While the latter expression can be rigorously derived for infinite-molecular-weight homopolymer,[1] there has been no equivalent justification for its application to the brush. This problem will not affect most SST predictions, but it will compromise those that rely upon an accurate treatment of finite-stretching corrections. In addition to autophobic dewetting,[8] this includes issues such as the effective interaction between opposing brushes[12] and certain phase behavior of block copolymer–homopolymer blends.[9–11] If SST is to be used for such problems, finite-stretching corrections need to be treated by a more rigorous means such as that introduced in Ref. 14.

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