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Finite extensibility and density saturation effects in the polymer brush

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Abstract. — We study the equilibrium statistics of flexible neutral polymer chains attached by one end onto a flat interface (the polymer « brush »). We account for the finite extensibility of the polymers, adopting a form for the free energy of a stretched chain that diverges as its fully-extended length is approached. Adopting also a Flory-Huggins equation of state for the local chemical potential, we obtain monomer density profiles and chain-end density distributions under various solvent conditions. We use an analytic self-consistent field approximation for long, highly stretched chains, as developed by Milner, Witten and Cates (Macromolecules 21 (1988) 2610), who found a parabolic density profile for brushes at « moderate densities » in a good solvent. Our work generalizes their approach to allow very high coverages and/or poor solvents to be considered; in each case the density profile is much flatter than a parabola.

1. Introduction.

The uniform grafting of monodisperse flexible neutral polymers onto a non-adsorbing substrate, immersed in solvents of different quality, is of both theoretical [1-20] and experimental [21-23] interest. An important use of the resulting polymer « brush » is in the steric stabilization of colloidal suspensions, with applications in waste-water treatment, in foodstuffs, pharmaceuticals, paints, etc. ; polymer coatings are also important in lubrication, adhesion, and related areas. It is apparent that optimal use of polymeric stabilizers entails
detailed investigation into the equilibrium of polymer brushes, since these play a direct role in
determining the interactions between coated particles in suspension.

Experimentally, grafted chains may be realised in several ways [21-22]. One method is to
use chains end-functionalised with (say) a zwitterionic group at one end which then attaches
itself to the substrate surface [22]. Another common procedure is to use an asymmetric
diblock copolymer AB, chosen so that the shorter A block adsorbs favourably onto the
substrate. Theoretical studies have been made for block-copolymers in selective and non-
selective solvents [19].

In previous theoretical treatments of terminally anchored chains [1-20], lattice models
energy balance arguments, scaling arguments and self-consistent field (SCF) methods were
employed. In this paper we shall use the SCF approach, as initiated by Dolan and
Edwards [3], later augmented by Helfand and Wasserman [24], and Scheutjens and Fleer [6].
This reduces the many chain problem to a single chain one involving a position dependent
chemical potential, which must be found self-consistently [25].

We exploit an analogy between the brush problem and one involving the motion of
fictitious classical-mechanical particles moving in an external field related to the chemical
potential. The correspondence between highly stretched chains and classical trajectories was
first exploited by Semenov [26] in the context of molten block copolymers. This analogy was
used extensively in recent papers by Milner et al. [15-17]. In reference [15], Milner, Witten
and Cates (MWC) showed that for a typical chain in the brush, the only configurations
contributing significantly are those that follow the « classical path » (of least « action » or free
energy) between the end-points of the chain. This holds because chains in a brush are highly
extended, at least in the long chain limit: the height h of the brush scales linearly with the
chain length N.

Adopting the usual Gaussian elasticity form for the stretching energy of a chain, MWC [15]
showed quite generally that for monodisperse chains the only stable form for the spatially
varying monomer potential is a parabola \( A - Bz^2 \), with \( z \) the distance from the grafting
surface). MWC restricted attention to the « moderate density » regime, defined as that in
which the « equation of state » relating the local chemical potential to the monomer density
reduces to a linear dependence. Clearly in this case the density profile is itself a parabola. At
low coverages, their results are in agreement with numerical calculations [27, 28] based on the
lattice SCF theories of Scheutjens and Fleer. The scaling laws relating brush height to surface
coverage and chain length, predicted by the full SCF treatment, are consistent with the energy
balance arguments of Alexander [5] who did not calculate the profile, instead making a simple
step function ansatz.

Departures are seen at high coverages, which is expected since the corresponding densities
are not moderate, but close to saturation (at volume fraction of polymer \( \phi \to 1 \)). At these
densities (and in any case to describe poor solvent conditions) it is necessary to use a more
realistic equation of state. For sensible results at high coverage, it is also essential to correct
for the finite extensibility of the chains. Indeed, it is easy to confirm that at high enough
coverage, retention of a Gaussian elastic term will always lead to predictions of the brush
height that exceed the fully-extended length of the chains.

In the present paper we rectify both of these shortcomings of the MWC theory. We adopt
for simplicity the Flory-Huggins equation of state, which allows for saturation and poor
solvent effects; and we choose a suitably modified elastic term that prevents unphysical chain
extension. Thus we are able to interpolate smoothly between the parabolic profile of MWC
and a flat, step-function profile which must obviously be recovered at coverage unity (when
each chain has no choice but to stretch to its fully extended length). Since we are dealing with
typical chain densities in the brush that are fairly high (a significant fraction of the saturation

density $\phi = 1$), we expect the SCF approach to be valid in all cases we consider. In section 2 we set out the theory to account for saturation and the finite extension of chains in the brush, and present the results obtained. Some final comments and conclusions are given in section 3.

2. Self-consistent mean field theory.

In this section we set up the 1-dimensional self-consistent equations describing the brush, appropriate for a flat geometry with translational invariance parallel to the grafting surface. As usual we adopt a structureless model [29] for the polymer chains since we are interested only in the macroscopic statistical properties. We adopt the same Lagrangian formalism as used by MWC [15]. The configurational sum $\Omega$ of all polymer chains, characterised by the positions $z_i(n)$, with $n = 0, 1, \ldots N$, of the ends of the $N$ monomer segments of the $i$-th chain is given by (working in units of $k_B T = 1$)

$$\Omega = \exp (- F(K)) = \sum_{\{z_i(n)\}} \exp (- (T + W))$$

(1a)

or in the continuum language

$$\Omega = \int d[z_i(n)] \exp (- (T + W))$$

(1b)

where $F(K)$ is the free energy for $K = \sigma A$ chains with $\sigma$ as the surface coverage ($\sigma = 1$ is saturation) and $A$ the grafted surface area; $T$ is the free energy of stretching of the chains and $W$ is their interaction energy.

$T$ is the sum of independent stretching energies $T_i$. Our model for $T_i$ which accounts for the finite chain extensibility is defined as

$$T_i = \int_0^N dn \frac{\gamma z_i^2(n)}{2(1 + |z_i(n)|)}$$

(2)

where $\dot{z}_i = dz_i/dn$ and $\gamma$ is a dimension-dependent parameter which we shall discuss later in detail. (MWC took $\gamma = 1$ [15]). We have chosen this form for $T_i$ in an ad hoc manner subject to the requirements that (i) it reduces to the usual Gaussian stretching form $\frac{\gamma}{2} \left( \frac{dz}{dn} \right)^2$ when $|\dot{z}| \to 0$; and (ii) it has a divergent derivative as $|\dot{z}| \to 1$. The second of these requirements enforces an extensibility limit at $|\dot{z}| = 1$; correspondingly a classical mechanical particle with $T_i$ as its Lagrangian would have a limiting speed of unity.

To have a stronger analogy with classical mechanics, it would be attractive to choose instead of (2) the Lagrangian of a relativistic particle. This choice was first proposed by Vilgis and Kilian in the context of rubber elasticity theory [30]; it leads to more complicated calculations than equation (2), as shown in appendix A. Various other functional forms can be obtained from specific local models of the chain at the monomer level [31]; however, we emphasize that there is no reason, a priori, for choosing one form over another (subject to requirements (i) and (ii) above). The corrections to Gaussian elasticity for polymers, though universally present, do not take a universal form, but should vary from one species of polymer to another [31]. With this in mind, the choice in (2) is motivated mainly by analytical convenience: it happens to lead to simple Laplace transform properties which we exploit below.

The remaining term in (1) is $W$, the interaction energy of the chains. It includes the segment-segment and segment-solvent interactions. In this paper we shall use the Flory-
Huggins lattice expression [29] for the free energy of mixing $F_{\text{mix}}$ per site, which for long chains reduces to

$$F_{\text{mix}} = (1 - \phi) \ln (1 - \phi) + \chi \phi (1 - \phi)$$  \hspace{1cm} (3)

where $\phi$ is the local monomer density and $\chi$ is as usual Flory's interaction parameter. In (3), $\phi(z)$ is defined in a self-consistent way as

$$\phi(z) = \sum_{i,n} \delta(z - z_i(n)).$$  \hspace{1cm} (4)

From (3) we have

$$W = \int dV \ F_{\text{mix}}.$$  \hspace{1cm} (5)

The change in the configuration sum (1) on addition of a test chain $j$ say, is given by

$$\Delta \Omega = \exp (- (F(K) - F(K - 1))) = \sum_{\{i_j(n)\}} \exp (- S_j)$$  \hspace{1cm} (6)

where the « action » $S_j$ is

$$S_j = \int_0^N dn \left\{ \frac{\gamma z_j^2(n)}{2(1 - |z_j(n)|)} - V(z_j(n)) \right\}$$  \hspace{1cm} (7)

and we introduce an « effective potential » $V(z_j)$ which is the negative of the space dependent monomer chemical potential. (The change in sign is introduced so that (7) looks like the Lagrangian of a particle in the potential $V$.)

2.1 THE CLASSICAL LIMIT TO THE SELF-CONSISTENT EQUATIONS. — When the brush is sufficiently dense that the chains are stretched far beyond their unperturbed gyration radii, the only path which contributes significantly to (6) for a chain $j$ is the one which minimizes the action $S_j$ at fixed positions for the chain ends. In the long-chain limit, perturbations about this stationary path can be ignored in (7). (These results of reference [15] are unaffected by our adoption of more general expressions for the equation of state and the stretching energy).

From (1), (2) and (5), the total free energy $F(K)$ of the brush is

$$F(K) = \sum_{i=1}^{K} \int_0^N dn \left\{ \frac{\gamma z_i^2(n)}{2(1 - |z_i(n)|)} \right\} + \int dV \ F_{\text{mix}}(\phi(z))$$  \hspace{1cm} (8)

where each of the chains separately minimizes (7). Suppose that in equilibrium the free ends of the brush are at height $\xi_i$ for $i = 1, 2, \ldots, K$. Then the change in free energy $\Delta F_i$ on adding a single chain $i$ while keeping all others fixed in space is

$$\Delta F_i = \int_0^N dn \left\{ \frac{\gamma z_i^2(\xi_i, n)}{2(1 - |z_i(\xi_i, n)|)} \right\} + \int dn \frac{\delta F(\phi(z_i))}{\delta \phi}.$$  \hspace{1cm} (9)

From (7) and (9) we relate the effective potential $V(z_i)$ to $F_{\text{mix}}$ via the functional derivative

$$V(z_i) = - \frac{\delta F(\phi(z_i))}{\delta \phi}.$$  \hspace{1cm} (10)
The minimisation condition of (8) is simply the set of Euler-Lagrange equations of the Lagrangian of the chains given by

\[ L(\{\dot{z}_i\}, \{z_i\}, n) = \sum_{i=1}^{K} T_i(\dot{z}_i) - V(z_i) = \sum_{i=1}^{K} L_i(\dot{z}_i, z_i) \]  

(11)

which is a sum over single chain Lagrangians \( L_i \). Hence each chain \( i \) satisfies (dropping the suffix \( i \))

\[ -\frac{\partial U(z)}{\partial z} = \frac{d}{dn} \left( \frac{dL}{dz} \right) = \frac{d}{dn} \left\{ \frac{\gamma}{2} \frac{\dot{z}(\zeta, n) + \dot{z}^2(\zeta, n)}{(1 - |\dot{z}(\zeta, n)|)^2} \right\} \]

(12)

where we have (for future convenience) decomposed the effective potential \( V(z) \) as

\[ V(z) = U(z) - A(h) + 1 - \chi. \]

(13)

In this expression, \( A(h) \) is a constant for fixed coverage \( \sigma \) (hence fixed equilibrium height \( h \)) and is chosen so that

\[ U(0) = 0 \quad \text{and} \quad U(N) = \infty. \]

(14)

2.2 THE EQUAL TIME REQUIREMENT. — The results of the preceding section specifically relate to our choice of (2) for the modified stretching energy but are independent of the form of the equation of state. As was found by MWC for the case of a Gaussian stretching energy, the problem of calculating \( V(z) \) simplifies dramatically if one assumes that the density of free chain ends is nonzero throughout the brush. Their proof [15] that this is indeed true for a Gaussian stretching energy carries over almost unchanged to the present case (see Appendix B). Thus the limiting case of a step function profile at coverage unity (for which all chain ends are at the front of the brush) is approached via a sequence of end-density distributions that remain nonzero everywhere.

Bearing in mind that the trajectory of a chain is found by minimizing the action \( S_j(7) \), we note that finding the configuration of a chain whose end happens to lie at height \( \zeta \) above the grafting surface is the same as that of finding the trajectory of a particle, with (7) as its Lagrangian, starting from rest at this position. (The initial velocity is zero since there is no external force on the chain end). Since all chains have the same length \( N \), our task is to find the form of the potential \( V(z) \) such that a particle starting anywhere within the brush will reach the wall in equal time, \( N \).

For a Gaussian stretching energy, the equal time potential is simply a parabola \( (V = - A + Bz^2) \) [15]. The problem of finding the potential for a particle with Lagrangian given by (7) requires a more detailed analysis, which we now give.

Since the single chain Lagrangian (11) does not explicitly depend on « time », \( n \), there exists a constant of the motion \( H \) [32] such that

\[ H = \dot{z} \frac{\partial L}{\partial \dot{z}} - L = \frac{\gamma z^2}{2(1 - |\dot{z}|)^2} + V(z). \]

(15)

We may equate this to the total energy \( V(\zeta) \), recalling that \( \zeta \) is the starting height of the chain. Therefore from (13) and (15) we obtain

\[ \dot{z}(\Delta U) = -\frac{1}{\kappa(\Delta U)} \]

(16a)

\[ \kappa(x) = (1 + \sqrt{\gamma / 2x}) \]  

(16b)
for the velocity \( \dot{z} \) of the particle at \( z \), where we have defined \( \Delta U = U(\zeta) - U(z) \). With these definitions the equal time constraint becomes

\[
N = \int_0^{\zeta - h} \text{d}z \mathcal{K}(\Delta U) .
\]  

(17a)

To calculate our potential \( U(z) \), it is convenient to use \( U \) itself as the integration variable [17]; equation (17a) may then be written

\[
N = \int_0^{U} \text{d}U' f(U') \mathcal{K}(U - U')
\]  

(17b)

where \( f(U') = \frac{\text{d}z}{\text{d}U'} \) is now the unknown function to be determined. For \( \Delta U \) small (17) reduces to

\[
N = \int_0^{U} \text{d}U' f(U') \sqrt{\frac{\gamma}{2(U - U')}}
\]  

which is the case of a Gaussian stretch energy; the analysis of MWC then follows in this limit and the potential approaches a parabola. (Note also from (16) that as \( \Delta U \to \infty \), \( |\dot{z}| \to 1 \), which imposes the required maximum extensibility of the chains).

2.3 FORM OF THE EFFECTIVE POTENTIAL. — Taking the Laplace transform of (17b) and inverting yields [33]

\[
f(U) = \frac{\text{d}z}{\text{d}U} = N \alpha \left\{ \frac{1}{\sqrt{\pi U}} - \alpha \exp(\alpha^2 U) \text{erfc}(\alpha \sqrt{U}) \right\}
\]  

(18)

where \( \alpha = \sqrt{2/\pi \gamma} \). Using the boundary conditions (14) gives

\[
z(U) = N \alpha \left\{ 2 \sqrt{\frac{U}{\pi}} - \frac{2}{\alpha} \int_0^{\sqrt{U}} \text{d}\beta \beta \exp(\beta^2) \text{erfc}(\beta) \right\} .
\]  

(19)

The inverse of this function (which can easily be found numerically) is the equal time potential \( U(z) \) for a particle with the Lagrangian of (7). Figure 1 shows a plot of \( U(z) \) versus distance in units \( z/N \). With (13) this specifies the effective monomer potential \( V(z) \). For \( z \ll N \), the parabolic form is recovered as expected, whereas \( U(z) \) diverges at \( z = N \).

To get from the monomer potential to a density profile, one must invoke an equation of state; in the Flory-Huggins approximation (using (3), (10) and (13)) we obtain

\[
U(z) = \ln \left( 1 - \phi(z) \right) + 2 \chi \phi(z) + A(h) .
\]  

(20)

By equating this to \( U(z) \) obeying (19), the density profile \( \phi(z) \) may now be constructed for various values of the parameter \( A(h) \). This generates a family of profiles \( \phi(z) \) corresponding to different brush heights. The corresponding values of the coverage \( \sigma \) may be found afterwards by integrating the density profile.

These procedures are implemented numerically, but this is fairly straightforward in view of our closed-form result for \( z(U) \). (We should note that the existence of a relatively simple expression for this function is what motivated our particular choice for the stretching term \( T_i \) in (2). The corresponding result for a « relativistic particle » Lagrangian is discussed in Appendix A and is more complicated).
2.4 DENSITY PROFILES: ATERMAL ($\chi = 0$) CASE. — The athermal case has a particularly simple form for $\phi(z)$. From (20) putting $\chi = 0$ gives for the local monomer density

$$\phi(z) = 1 - \exp(U(z) - A(h)).$$

The constant $A(h)$ is fixed by the conservation of material, which requires

$$\int_0^h dz \phi(z) = N \sigma.$$  

We now argue that the equilibrium brush corresponds to one in which the monomer density vanishes smoothly, rather than discontinuously, at the front of the brush. This was shown for the parabolic profile by MWC [15]; their argument generalizes in a straightforward manner so long as $F_{\text{mix}}(\phi)/\phi$ is a monotonically decreasing function of $\phi$. This holds throughout the good solvent regime ($\chi \leq 1/2$) but fails in poor solvents as we will discuss in section 2.7.

Since for $\chi = 0$ there is no step discontinuity at the front of the brush, we may set $\phi(h) = 0$ and thus determine $A(h)$ to obey

$$\exp(-A(h)) = \exp(-U(h)) = \frac{h - N \sigma}{\int_0^h dz \exp U(z)}.$$  

Equations (21) and (23) determines the brush profile: (21) gives the profile as a function of the parameter $A(h)$, and (23) fixes this parameter in terms of coverage $\sigma$ corresponding to an equilibrium height $h$.

The dependence of $h$ and $\phi(0)$ for $\gamma = 1$ on $\sigma$ is shown in figure 2. At small $\sigma$ these show characteristic $\sigma^{1/3}$ and $\sigma^{2/3}$ behaviours respectively, which were predicted in previous treatments [4, 7, 15]. As coverage approaches saturation, $h$ becomes almost linear in $\sigma$; in this limit, the brush can crudely be thought of as a slab of material at maximum density, whose height therefore increases linearly with coverage. Figure 3a shows normalised density profiles with $\gamma = 1$ for various coverages in the athermal brush. The familiar parabolic form is only
Fig. 2. — Monomer density $\phi(0)$ and equilibrium height $h/N$ versus coverage $\sigma$ represented by dotted and solid curves respectively.

Fig. 3. — (a) Normalised monomer density $\phi(z)/\phi(0)$ profiles versus normalised height $z/h$ of the present theory for various coverages $\sigma = 0.025, 0.25, 0.50$ and 0.70 corresponding to solid, dotted, dashed and dotted-dashed curves respectively. (b) End probability density $\varepsilon(z)$ profiles versus normalised height $z/h$ for coverages $\sigma = 0.025, 0.25$ and 0.50 represented by solid, dotted and dashed curves respectively. The curves are scaled by $\varepsilon_{\text{max}}$, the maximum value of $\varepsilon(z)$. Corresponding values of $\varepsilon_{\text{max}}$ for the three coverages are 6.7, 5.8 and 8.5 respectively.

recovered at rather low coverages ($\sigma < 0.025$); this is not surprising since the corrections to Gaussian elasticity enter whenever $h/N$, which varies as $\sigma^{1/3}$, is a significant fraction of unity. For higher $\sigma$ the profile becomes gradually flatter, as expected. Note that since the elasticity corrections are largest for the most extended chains, the first significant departure from the parabolic form, as $\sigma$ is increased, is a steepening in the falloff at the front of the brush.
2.5 Determination of the end distribution. — In this section we consider how the chain ends are distributed through the brush. As discussed already in section 2.2 and Appendix B, we expect a continuous end-density, which should however approach a delta-function at the front of the brush in the limit \( \sigma \to 1 \) (when all chains are fully stretched).

Define the probability that a chain end in a brush of height \( h \) lies between \( \zeta \) and \( \zeta + \Delta \zeta \) as

\[
\varepsilon(\zeta ; h) \, d\zeta .
\]

Now the monomer density \( \phi(z) \) is simply the sum of contributions \( |dn/dz_i| \) that each chain \( i \) starting at \( z_i \) makes at position \( z \) i.e.

\[
\phi(z) = \sigma(h) \int_{\zeta}^{h} d\zeta \, \varepsilon(\zeta ; h) \left| \frac{dn(z, \zeta ; h)}{dn} \right|^{-1} .
\]

Note that, as shown in reference [15], chains starting at \( \zeta < z \) do not contribute to (25). In the particle analogue the term inside the modulus is simply the velocity. Using (16) and transforming to potential \( U \) as the integration variable (25) becomes, with \( U_0 = U(h) \)

\[
\phi(U) = \sigma(U_0) \int_{U_0}^{U} dU' \, \bar{\varepsilon}(U' ; U_0) \left( 1 + \frac{\gamma}{\sqrt{2(U' - U)}} \right)
\]

where \( \phi(U) = \phi(z(U)) \) and \( \bar{\varepsilon}(U ; U_0) \) denotes the end density in « potential space » [17]. Inverting (26) for \( \bar{\varepsilon}(U ; U_0) \) yields the end probability distribution as

\[
\bar{\varepsilon}(U ; U_0) = \int_{U_0}^{U} dU' \, \frac{d\phi(U')/dU'}{\sigma(U_0)} \left\{ \frac{1}{\pi} \sqrt{\frac{2}{\gamma(U' - U)}} - \frac{2}{\pi \gamma} \exp \left( \frac{2(U' - U)}{\pi \gamma} \right) \text{erfc} \left( \frac{2(U' - U)}{\pi \gamma} \right) \right\} .
\]

To obtain the end-density in real space we may write \( \varepsilon(z ; h) = \bar{\varepsilon}(U ; U_0)(dU/dz) \) where \( dz/dU \) obeys (18). The resulting end-density distributions for the athermal brush are shown in figure 3b for various coverages. As with the monomer density profile, the asymptotic form \( \varepsilon(z ; h) = (3/h^3) z (h^2 - z^2)^{1/2} \) predicted by MWC is recovered only at very low coverages. For \( \sigma > 0.1 \) the curves show pronounced upward curvature and an emphatic peak near the front of the brush. For example, with \( \sigma = 0.5 \) roughly 45% of the ends lie in the front 10% of the brush; the corresponding figure at low coverages, \( \sigma = 0.025 \) is 12%.

In figures 4a-d we compare the results of this and the previous section with those found from a numerical mean-field approach based on Scheutjens-Fleer theory, using chains of 100 steps on a simple cubic lattice in three dimensions and a Flory-Huggins equation of state. (The lattice data was kindly provided by Milner [34]). To make a quantitative comparison, we must select a value of \( \gamma \) in equation (2). This may be done by comparing the equilibrium end-to-end distance of a chain with its fully stretched length. The latter is equal to \( N \) on a unit cubic lattice in any dimension, presuming the direction of extension to coincide with a cubic axis. Thus to reproduce the well known result \( \langle R^2 \rangle = N \) for the end-to-end distance we must set \( \gamma = d \), the dimension of space. In figure 4 we present curves for \( \gamma = 3 \) and also for \( \gamma = 1 \) (as would be appropriate for a strictly one dimensional theory).

We see that for a low coverage, \( \sigma = 0.05 \), the \( \gamma = 3 \) profile compares well with the numerical result whereas for higher coverages our results based in equation (2) give a somewhat shorter brush than the lattice calculations. Indeed, the choice \( \gamma = 1 \) gives a closer
Fig. 4. — (a)-(b) Monomer density $\phi(z)$ and end probability density $\varepsilon(z)$ profiles versus height $z/N$ respectively for $\sigma = 0.05$. The solid and dashed curves correspond to dimension-dependent parameter $\gamma = 3$ and $\gamma = 1$ respectively. The dotted curve is the lattice mean field result based on the Scheutjens-Fleer theory. (Data for the lattice mean field are for 100 monomers per chain kindly provided by Milner). (c)-(d) Monomer density $\phi(z)$ and end probability density $\varepsilon(z)$ profiles versus height $z/N$ respectively for $\sigma = 0.25$.

agreement in this case. These differences give an indication of the degree of nonuniversality for strong-stretching corrections to the Gaussian elastic limit. There is no reason to prefer one type of calculation over the other, since the use of a lattice is at least as arbitrary as the introduction of equation (2). (Indeed, large changes in the profiles at high coverages would result if one merely rotated the lattice through 45 degrees with respect to the grafting surface!) One notable advantage of our method is that results can easily be obtained for
coverages close to unity, where the profile approaches a step-function (see e.g., Fig. 3). The corresponding calculations using the lattice SCF approach are extremely slow to converge [34], because of the high osmotic pressures near the wall, and the sharply peaked end distribution [35]. (The practical limit for these calculations seems to be near $\sigma = 1/2$ [34]).

2.6 FREE ENERGY OF FREE AND COMPRESSED BRUSHES. — It is shown in appendix B that in equilibrium the action $S_i$ (7) takes, for fixed coverage, the same numerical value for all chains in the brush. The free energy of the brush may then be obtained as follows. Selecting a chain near the surface, we get

$$S_i = -N V(0) = N (A(h) - 1 + \chi).$$ (28)

Constructing the brush by progressively adding chains, the free energy, $F_\sigma$, for some fixed $\sigma$, corresponding to an equilibrium height $h$ is

$$F_\sigma = \int_0^\sigma d\sigma' S(\sigma') = N \int_0^\sigma d\sigma' (A(h) - 1 + \chi)$$ (29)

where $A(h)$ satisfies (20). For illustrative purposes, we restrict attention to the athermal case $\chi = 0$. Using (23) and (29) we obtain

$$F_\sigma = N \int_0^\sigma d\sigma' \left[ \ln \left\{ \frac{g(h)}{h - N\sigma'} \right\} - 1 \right]$$ (30)

where $g(h) = \int_0^h dz \exp U(z)$. The non-athermal case may be treated using similar arguments.

We now consider the case of a brush compressed against a hard wall, or equivalently, another brush [15]. Clearly we can expect repulsive forces on compression to a height $z < h$, $h$ being the equilibrium height for some coverage, $\sigma(h)$. The integration in (30) is now performed in two steps. Firstly the brush is built up until the equilibrium height is $z(\sigma)$, say, corresponding to some $\sigma(z)$; from (30) we have

$$F_{1\sigma} = N \int_0^{\sigma(z)} d\sigma' \left[ \ln \left\{ \frac{g(h(\sigma'))}{h(\sigma') - N\sigma'} \right\} - 1 \right].$$ (31a)

The second step of the integration is to fix the height $z$ and increase the coverage from $\sigma(z)$ to $\sigma(h)$. Therefore we have

$$F_{2\sigma} = N \int_{\sigma(z)}^{\sigma(h)} d\sigma' \left[ \ln \left\{ \frac{g(z)}{z - N\sigma'} \right\} - 1 \right].$$ (31b)

The free energy of the compressed brush is

$$F_\sigma(z) = F_{1\sigma} + F_{2\sigma}.$$ (31c)

We obtain the compression force for $z < h$ in the athermal case $\chi = 0$ as

$$\Pi(z) = -\frac{dF_\sigma(z)}{dz} = -N \left[ \frac{\exp U(z)}{g(z)} (\sigma(h) - \sigma(z)) + \frac{1}{N} \ln \left\{ \frac{z - N\sigma(h)}{z - N\sigma(z)} \right\} \right].$$ (32)

The force curves found in this way for various $\sigma$ are shown in figure 5.
**2.7 OTHER SOLVENT CONDITIONS.** — The case of $\chi$ finite and less than 1/2 defines the good solvent regime. The mean field approach is valid for sufficiently high $\sigma$ and the non-Gaussian stretching energy is important. The results for the $\chi = 0$ case, as given above, are representative. More generally, from (20) we get

$$\frac{1 - \phi(z, h)}{\phi(z, h)} \exp(2\chi \phi(z, h)) = \exp(-\Delta U).$$

Equation (33) may be solved numerically by fixing $h < N$. Using (19), $\Delta U$ is known for all $z$, hence the density profile $\phi(z)$ can be found by solving the transcendental equation (33). The surface coverage $\sigma$ can be inferred from (22).

One special case, namely behaviour in a theta solvent ($\chi = 1/2$) at low coverage may be obtained by replacing the Flory-Huggins equation of state with a three body potential ($V \propto \phi^2$). This gives an elliptical profile rather than a parabolic one with vertical asymptote at the front of the brush.

The bad solvent case ($\chi > 1/2$) is more subtle. In this regime there is a discontinuity at the front of the brush, which means that (23) is no longer valid. To see why this arises, we recall [29] that the equation of state $F_{\text{mix}}(\phi)$ given by (3) for such a solvent exhibits an instability. There is an optimal volume fraction $\phi^*$ for which $F_{\text{mix}}/\phi$ is minimized:

$$\frac{\partial}{\partial \phi} \left( \frac{F_{\text{mix}}}{\phi} \right)_{\phi^*} = 0$$

$$\log(1 - \phi^*) + \chi \phi^{*2} + \phi^* = 0.$$  

A bulk polymer solution at $\phi < \phi^*$ will phase separate into a state of $\phi = \phi^*$ coexisting with a state of $\phi = 0$. (This holds in the limit $N \to \infty$, which has already been taken in (3)).

Clearly then, a brush profile which vanishes continuously at the front edge is locally unstable in a bad solvent ($\chi > 1/2$): both the osmotic term and the stretching energy favour collapse of any region at the front of the brush that has $\phi < \phi^*$. In fact, the proper boundary condition at the front of an unconstrained brush is in general that of zero osmotic pressure.
\( \phi \frac{\partial (F_{\text{mix}}/\phi)}{\partial \phi} \), which corresponds to a local density \( \phi = \phi^* \). (This may be checked by considering the force on a confining plate pressed against the brush: this is equal to the osmotic pressure at the front of the brush [15] and must vanish in equilibrium).

Using (20) this redefines the boundary condition for \( A(h) \) as

\[
A(h) = U(h) - \log \left( 1 - \phi^* \right) - 2 \chi \phi^* \tag{35}
\]

which yields for the brush profile

\[
\exp\left( 2 \chi \phi(z, h) \right) (1 - \phi(z, h)) = \exp(-\Delta U) \exp c \tag{36}
\]

where \( c = \log \left( 1 - \phi^* \right) + 2 \chi \phi^* \).

---

**Fig. 6.** — (a)-(c) Effects of solvent quality on the brush density profile \( \phi(z) \) versus height \( z/N \) for coverages \( \sigma = 0.025, 0.25 \) and 0.50 respectively. The solid, dashed and dotted curves correspond to Flory interaction parameter \( \chi = 0.75, 0.50 \) and 0.10 respectively.
The effects of varying solvent quality for various fixed $\sigma$ are shown in figure 6a-c. In particular we note that for $\chi = 1/2$ (theta solvent case) the profile goes continuously to zero with vertical slope at the front of the brush for the three coverages. At the lowest coverage, an elliptical profile is approached as predicted above. For $\chi > 1/2$ the brush as expected is relatively compact (since chains attract each other) although the brush height remains proportional to the chain length $N$ [36]. This ensures that the chains are strongly stretched even in a poor solvent, so that results based on the classical limit of the SCF equations remain reliable.

3. Conclusions.

In this paper we have generalized and extended the analytical SCF approach to polymer brushes as introduced by Milner et al. in reference [15]. The more complicated chain Lagrangian studied here lead to a somewhat less tractable analytical structure, which means that some numerical work is required to obtain profiles from the theory. Nonetheless our approach, which starts from the strong stretching (« classical ») limit of the SCF equations, is quite different in spirit from one involving the full numerical solution of the self-consistent problem as typified by the Scheutjens-Fleer approach [6, 27, 34]. The main aim of our work is to allow higher surface coverages and chain densities to be described within the MWC formalism. Our results reduce to those of reference [15] at low enough surface coverages, and interpolate all the way to the step-function profile of a completely saturated surface. One might expect that in this limit, some of our results for force profiles could be obtained by a suitable modification to the energy balance arguments of Alexander [5], which were based on a step-function profile. However, this turns out to be difficult since the Flory-Huggins interaction becomes a very strong function of density, and small departures from a flat profile become very important energetically. By decreasing solvent quality we may also approach the limit of a brush whose density is constrained to be constant, as arises in surfactant bilayers, for example [11, 36, 37].

To obtain reasonable results in high coverage regimes it is essential to include not only a realistic equation of state, but also corrections to the Gaussian stretching energy used by MWC. A drawback of our work is that the nonlinear stretching energy chosen (Eq. (2)) and the Flory-Huggins equation of state both involve ad-hoc approximations of restricted universality. In principle it would be possible to include more precise forms in each case, although the mathematics rapidly becomes more complicated (see, e.g., Appendix A). A measure of the « error bar » inherent in our work is seen in figure 4 where there are significant departures between our predictions and those of Scheutjens/Fleer type calculations [34] at coverages of order $\sigma = 0.25$. We expect the main difference between the lattice calculations and our own to relate to the choice of stretching term in equation (2), and while it would certainly be interesting to implement our SCF calculations for several different choices of this term [30, 31], that lies beyond the scope of the present work. We emphasize in any case that lattice-based models have no more claim to fundamental validity than our own equation (2), and indeed that the results for different lattices vary significantly [28, 34]. A major advantage of our approach is that results can easily be obtained for coverages right up to unity, in contrast to the convergence difficulties encountered by lattice calculations for coverages larger than about 1/2 in the athermal case [34, 35]. Even greater advantages are expected in poor solvent conditions.

Finally we point out that the original MWC theory, which involves a Gaussian stretching term and a quadratic equation of state ($F(\phi) \sim \phi^2$), yields brush heights that are a significant fraction of the fully extended height even at very low coverages. (For example $\sigma = 0.05$ yields $h/N \approx 0.4$ [15]). Since the polymer density near the wall scales as $\sigma^{23}$ (in contrast to
\( \sigma^{1/3} \) for the brush height), there is at best a limited regime in which the density is high enough for a mean-field approach to be suitable, but the brush height is small enough for non-Gaussian corrections to the stretching term to be negligible. In this sense our extension of the theory to « high » coverages is relevant to coverages that would normally be considered rather small. Note also that the main influence of the non-Gaussian corrections at low \( \sigma \) is to make the density profile vanish more steeply at the front of the brush than would otherwise be the case, which give a relative « hardening » of the force/distance profiles for compressed brushes. For force/distance curves, the earlier MWC theory is at the stage of (almost) parameter-free fits to experiment in certain systems at very low coverage [22, 38]. We may therefore hope for quantitative experimental tests for some of our new results in the near future.

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Appendix A.

It is interesting to compare the form of the kernel (16) (which results from adopting equation (2) as the stretching energy) to that of a relativistic particle. The Lagrangian for such a particle (with \( mc^2 = 1 \)) in one dimension acted on by conservative forces independent of \( \dot{z} \) is the familiar [31]

\[
L = - \sqrt{1 - \dot{z}^2} - V(z)
\]

from which the total energy of the particle is

\[
E = \frac{1}{\sqrt{1 - \dot{z}^2}} + V(z).
\]

Following (17) we get

\[
N = \int_0^U dU' \tilde{K}(U - U') f(U')
\]

where

\[
\tilde{K}(x) = \frac{1}{\sqrt{1 - (1 + x)^{-2}}}.
\]

Taking Laplace Transforms gives an algebraic equation which on inversion yields

\[
\frac{dz}{dU} f(U) = \mathcal{L}^{-1} \left[ \frac{N}{sK_1(s) \exp s} \right]
\]

where \( \mathcal{L} \) is the Laplace operator and \( K_1 \) is the modified Bessels function of the second kind of order one.

This form of \( f(U) \) is less tractable than (18) which is our main reason for adopting equation (2) for the stretching energy rather than \( T = - \sqrt{1 - \dot{z}^2} \) as might be suggested by the above relativistic analogy.
Appendix B.

In this appendix we give arguments, directly generalizing those of reference [15], which establish that the end density in a brush is everywhere nonzero and that the action of every chain in the brush is the same.

We start by establishing the local stability of a brush whose chains obey the classical equations of motion arising from the action (7). For the brush to be stable, the minimum of the action $S_j$ from (7) should be stationary with respect to changes to the end position:

$$\frac{\partial S_i(\xi_i)}{\partial \xi_i} = 0 \quad \forall i \quad \text{where} \quad 0 < \xi_i < h.$$ 

Using the single chain Lagrangian (7) and (12) we get (dropping the suffix)

$$\frac{\partial S}{\partial \xi} = \int_0^N dn \left[ \frac{\partial z}{\partial \xi} \frac{\partial L}{\partial z} - \frac{\partial z}{\partial \xi} \frac{\partial V(z)}{\partial z} \right] = \int_0^N d \left[ \frac{\partial z}{\partial \xi} \frac{\partial L}{\partial z} \right] = \frac{\partial z(n)}{\partial \xi} \frac{\partial L}{\partial z} \bigg|_0^N.$$ 

At the lower limit, $\frac{\partial z}{\partial \xi}(0) = 0$ since $z(0) = 0$ (there is no force on a free chain end), and at the upper limit, $\frac{\partial z}{\partial \xi}(N) = 0$ since all particles terminate at the wall. Thus $S(\xi)$ is indeed stationary with respect to small changes in the position of a chain end.

This implies that $S(\xi)$ is constant in any interval of $\xi$ where chain-ends are found. The action $S$ is thus the same for every chain (as assumed in Sect. 2.6) so long as the end-density is everywhere nonzero. To establish this, let us consider a hypothetical « dead zone » [15] in which no ends are present. From equation (25), and using the conservation of energy (Eq. 15)), we find that a self-consistent solution for the density in such a dead zone is one in which the $\phi$ is a constant throughout the zone. Consider now a chain whose free end is at the outer edge front of the zone. If we bring this free end slightly towards the wall (so that it lies within the dead zone), then $S$ for that chain decreases, since stretching energy is released at no cost in osmotic free energy. Alternatively, we may observe that such a chain must have an initial velocity toward the wall so as to arrive there in equal time to a particle starting from the inner edge of the zone. From the expression for $\frac{\partial S}{\partial \xi}$ derived above (and using also (12)) this inward initial velocity (negative) implies a positive value of $\frac{\partial S}{\partial \xi}$, so that moving the chain end towards the wall lowers the free energy of the system. This shows that dead zones are locally unstable, and it follows that the end density is nonzero throughout the brush.

References

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