Classical Theory of Polymer Brushes

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We derive from the self-consistent field equations the classical theory of polymer brushes. It results from ignoring, for each position of the polymer end point, all but the most probable configuration. Results for the brush density profile and polymer end distribution depend sensitively on the square of the ratio of the characteristic brush height to the polymer radius of gyration, β. For finite β, the monomer density exhibits a Gaussian tail and the polymer end-points are stetched. In the limit of infinite β, this classical theory reduces to that of Milner *et al.* and Zhulina *et al.*

At high surface coverage one finds that polymer chains grafted at one end to a surface are strongly stretched and form a polymer brush. After the early work by Alexander [?] and de Gennes [?], Semenov [?] observed that this strong stretching implies that fluctuations around the most probable, or "classical", paths are unimportant. Milner et al. [?] and Zhulina et al. [?] implemented this idea in the limit of infinitely strong stretching, i.e., in the limit in which the brush height is infinitely larger than the unperturbed polymer radius of gyration. Results include a density profile which is parabolic, a polymer end distribution which is non-zero only for a finite range of distances from the grafting surface, and a universal form for all polymer paths which are unstretched at their free end, and which differ only in their amplitude. Except in this limit of infinitely strong stretching, formulation of the classical theory, which results from ignoring all polymer configurations other than the most probable, has received little attention [?]. A recent attempt to do so in an approximate fashion [?] produced density profiles for a strongly, but finitely stretched, system which were closer to those calculated from the full self-consistent theory than were the results of [?,?] for the limiting case of an infinitely stretched system. This indicated that a classical theory might yield rather good results for brushes over some non-zero range of polymer stretching. In this Letter we derive the classical theory for polymer brushes and show that it not only yields useful results over a wide range of the stretching parameter, but also provides unexpected insights as well. In particular we find that, in general, (i) the density profile has a Gaussian decaying tail, (ii) the end-point distribution is non-zero everywhere, (iii) classical paths with different end points are different, (iv) paths with endpoints beyond a certain distance from the grafting surface proceed monotonically to the grafting surface, and are stretched throughout their entire length, including the endpoint, (v) paths with endpoints within that distance initially proceed *away* from the grafting surface, reach a maximum, and then continue to the surface. They are stretched everywhere except at the maximum[1]. As it should, the classical theory reduces, in the limit of infinite stretching, to that of Refs. [?,?].

We begin with the partition function for n Gaussian polymers of N units end-grafted to an area A interacting via a quadratic repulsion with excluded volume w

$$Z = \prod_{\alpha=1}^{n} \left[\int \mathcal{D}\mathbf{r}_{\alpha}(\cdot) \exp\left\{ -\frac{3}{2a^2} \int_0^N ds\, \dot{\mathbf{r}}_{\alpha}^2(s) \right\} \right] \exp\left\{ -\frac{w}{2} \int d\mathbf{r}\, \hat{\Phi}^2(\mathbf{r}) \right\}. \tag{1}$$

The Kuhn length is denoted by a, and the monomer density is defined by $\hat{\Phi}(\mathbf{r}) = \sum_{\alpha=1}^{n} \int_0^N ds\, \delta[\mathbf{r} - \mathbf{r}_{\alpha}(s)]$. We insert the identity $1 = \int \mathcal{D}\Phi \delta(\Phi - \hat{\Phi})$, use the integral representation of the delta function, $\delta(\Phi - \hat{\Phi}) = \int \mathcal{D}\Omega \exp \int \Omega[\Phi - \hat{\Phi}] d\mathbf{r}$, and carry out the Gaussian integration over Φ. This yields $Z \sim \int \mathcal{D}\Omega \exp(-A\sigma F[\Omega])$, with $F[\Omega] = -\int dz \Omega^2(z)/2w\sigma - \ln \mathcal{Q}[\Omega]$ where $\mathcal{Q}[\Omega]$ is the partition function of a single polymer in an external field Ω. We have assumed that the coverage $\sigma = n/A$ is sufficiently great that the field depends only on the vertical coordinate z which measures the distance from the grafting surface. Note that with this assumption the free energy per polymer is given exactly by the minimum value of $F[\Omega]$ in the thermodynamic limit of infinite A [?]. This value is, by definition, that given

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[1] These results have been compared with detailed self-consistent field-theory calculations [?]. We find full agreement concerning the polymer path characteristics, and also, for stretching which is not too small, good quantitative agreement for the calculated monomer density profiles and end-point distributions.

by self-consistent field theory, and occurs for the field, ω, obtained from the solution of the self-consistent equation $\omega(z) = -\sigma w \delta \log \mathcal{Q}[\omega]/\delta\omega = w\phi(z)$, where ϕ is the ensemble average of the monomer density.

The mean-field free energy per polymer in units of $k_B T$ is

$$F = -w \int_0^\infty \mathrm{d}z \; \phi^2(z)/2\sigma - \ln \mathcal{Q}. \tag{2}$$

Although the single particle partition function can be calculated exactly numerically [?,?], it is of interest to determine the classical approximation which retains, for each position of the polymer end point, only the most probable polymer configuration. To make this approximation clear, we change the variable describing the polymer path from $z(s, z_0)$ with $z(0, z_0) = z_0$, $z(N, z_0) = 0$ to $s(z, z_0)$ with $s(z_0, z_0) = 0$, $s(0, z_0) = N$, and define $E(z, z_0) = -[ds(z, z_0)/dz]^{-1}$. Anticipating that paths which start at a z_0 very near the grafting surface may first move away from the surface before returning to it, we define $z_m(z_0)$ to be the largest value of z attained by a path which begins at z_0. The single particle partition function can then be written

$$\mathcal{Q} = \int_0^\infty \mathrm{d}z_0 \int' \mathcal{D}E(\cdot, \cdot) \exp\left\{ -\int_0^{z_m(z_0)} \mathrm{d}z \left[\frac{3}{2a^2}|E(z, z_0)| + \frac{w\phi(z)}{|E(z, z_0)|} \right] \right\}. \tag{3}$$

The functional integral over all stretching functions E selects only those which satisfy the constraint that all polymer paths have the same length. The self-consistent equation for the density follows from functional differentiation, $\phi(z) = -\sigma\delta \log \mathcal{Q}/\delta w\phi$.

The classical approximation consists of replacing the functional integral over the E in Eq.(??) by the integrand evaluated with the function $e(z, z_0)$ which extremizes the mean-field free energy F, thereby eliminating all but the most probable path for a given z_0.

The self-consistent equation which determines the density becomes, in this classical limit,

$$\phi(z) = \frac{\sigma}{\mathcal{Q}} \int_{z_0(z)}^\infty \frac{\mathrm{d}z_0}{|e(z, z_0)|} \exp\left\{ -\int_0^{z_m(z_0)} \mathrm{d}z' \left[\frac{3}{2a^2}|e(z', z_0)| + \frac{w\phi(z')}{|e(z', z_0)|} \right] \right\}, \tag{4}$$

where $z_0(z_m)$ is the inverse of $z_m(z_0)$. By comparison with the constitutive relationship between the end-point distribution $g(z_0)$ and the density,

$$\phi(z) = \int_{z_0(z)}^\infty \mathrm{d}z_0 \; \frac{g(z_0)}{|e(z, z_0)|}, \tag{5}$$

the end-point distribution is found to be

$$g(z_0) = \frac{\sigma}{\mathcal{Q}} \exp\left\{ -\int_0^{z_m(z_0)} \mathrm{d}z \left[\frac{3}{2a^2}|e(z, z_0)| + \frac{w\phi(z)}{|e(z, z_0)|} \right] \right\}. \tag{6}$$

From this equation one obtains a simple expression for $-\ln \mathcal{Q}$, a quantity which is, of course, independent of z_0. The expression is made particularly transparent by multiplying it by $g(z_0)$, integrating over all z_0, and using the normalization $\int \mathrm{d}z_0 \; g(z_0) = \sigma$. One obtains

$$-\ln \mathcal{Q} = \int_0^\infty dz_0 \frac{g(z_0)}{\sigma} \int_0^{z_m(z_0)} dz \left[\frac{3}{2a^2}|e(z, z_0)| + \frac{w\phi(z)}{|e(z, z_0)|} \right] + \int_0^\infty dz_0 \frac{g(z_0)}{\sigma} \ln\left(\frac{g(z_0)}{\sigma} \right), \tag{7}$$

which is the free energy of a single polymer in an external field $w\phi$. Finally, substituting this into Eq.(??), we obtain the desired expression for the free energy of the many-polymer system. We choose to write it in terms of the dimensionless coordinate $\bar{z} = z/\hat{z}$ with $\hat{z} \equiv [N(2w\sigma a^2/3)^{1/3}]$, the rescaled density $\bar{\phi}(\bar{z}) \equiv \phi(z)\hat{z}/(N\sigma)$ and endpoint distribution function $\bar{g}(\bar{z}_0) \equiv g(z_0)\hat{z}/\sigma$ which satisfy the normalizations $\int \mathrm{d}\bar{z} \; \bar{\phi}(\bar{z}) = 1$ and $\int \mathrm{d}\bar{z}_0 \; \bar{g}(\bar{z}_0) = 1$ respectively, and the rescaled stretching function $\bar{e}(\bar{z}, \bar{z}_0) \equiv e(z, z_0)N/\hat{z}$. The result for the free energy per polymer in units of $k_B T$ in the classical limit is, to within an unimportant constant,

$$\frac{F}{\beta} = -\frac{1}{2} \int_0^\infty \mathrm{d}\bar{z} \; \bar{\phi}^2(\bar{z}) + \int_0^\infty \mathrm{d}\bar{z}_0 \; \bar{g}(\bar{z}_0) \int_0^{\bar{z}_m(\bar{z}_0)} \mathrm{d}\bar{z} \left[|\bar{e}(\bar{z}, \bar{z}_0)| + \frac{\bar{\phi}(\bar{z})}{|\bar{e}(\bar{z}, \bar{z}_0)|} \right] + \frac{1}{\beta} \int_0^\infty \mathrm{d}\bar{z}_0 \; \bar{g}(\bar{z}_0) \ln[\bar{g}(\bar{z}_0)] \tag{8}$$

where $\beta \equiv N(3w^2\sigma^2/2a^2)^{1/3}$ is the square of the ratio of the typical brush height $\hat{z}$ to that of the unperturbed polymer radius of gyration $a\sqrt{N}$. The last term in the free energy is easily recognized to be the entropy associated with the

end-point distribution. Just such a term was introduced in order to study the dynamics of polymer brushes [?] and, more recently, in the context of strongly segregated polymer melts [?]. The present calculation furnishes a simple derivation of this important term. When this free-energy is extremized with respect to the density $\bar{\phi}(\bar{z})$ and end-point distribution $\bar{g}(\bar{z}_0)$, subject to their normalizations, rescaled versions of Eqs. (??) and (??) are obtained. Variation with respect to $\bar{e}(\bar{z}, \bar{z}_0)$ subject to the equal-length constraint $\int_0^{\bar{z}_m(\bar{z}_0)} d\bar{z}/|\bar{e}(\bar{z}, \bar{z}_0)| = 1$ yields

$$\bar{e}^2(\bar{z}, \bar{z}_0) = \bar{\phi}(\bar{z}) - \bar{\phi}(\bar{z}_0) + \bar{\pi}^2(\bar{z}_0) \tag{9}$$

The physical meaning of the Lagrange multiplier π is the magnitude of the stretching of the polymer at its free endpoint.

In the limit in which $\beta \to \infty$, the entropy term can be neglected, and the free-energy is minimized by the asymptotic classical solution given in Refs [?,?]. At finite β, the results are markedly different[2]. They are summarized in Fig. 1. Density profiles for four different values of β, plotted in Fig. 1a), approach the asymptotic parabolic solution (shown as a thick dashed line) as β increases. The profiles for finite β show a Gaussian tail, and deviate substantially from the parabolic shape as β decreases. Figure 1b) shows the corresponding end-point distributions $\bar{g}$, which again approach the asymptotic result (shown as a thick dashed line) as β increases. The entropic term forces $\bar{g}$ to be non-zero everywhere for finite β and leads to a rather uniform end-point distribution for small β.

The classical paths are, in general, stretched everywhere including their endpoint. Fig. 1c) shows, for four values of β, the function $\bar{e}(\bar{z}_0, \bar{z}_0)$ whose magnitude is the stretching at the endpoint. Not surprisingly, those few paths which start far from the surface are greatly stretched there. The negative value of $\bar{e}$ for paths which start close to the surface indicates that these paths initially move away from the surface before turning back. Fig. 1d) shows the difference between the maximum value $\bar{z}_m$ which these paths attain and their end-point value.

The above is the classical theory of polymer brushes. The conditions of applicability of the theory are obviously important. The approximations we have made limit the applicability of the theory in different ways. The essential ones are to ignore density fluctuations, which is mean-field theory, and to ignore all but the most probable polymer configurations, which is the classical approximation. Validity of the former requires that the chains are Gaussian on all length scales, i.e., that the Gaussian blobs are larger than the Pincus blobs, which is satisified for $w^2/a^6 \ll \sigma a^2$. We note that the inverse grafting density can not exceed the monomer area, i.e., $\sigma a^2 < 1$. The validity of the classical approximation requires that the chains be strongly stretched, $\hat{z}/aN^{1/2} = (2\beta/3)^{1/2} > 1$. Using the definition of β above, we can conveniently write these three conditions as

$$1/\sigma^2 a^4 N^3 < w^2/a^6 \ll \sigma a^2 < 1. \tag{10}$$

As noted in Ref. [?], the excluded volume w should be large, but not too large, in order for a classical theory to be applicable. As can be seen from Fig. 1c) the chains are not stretched equally, and we expect that the classical profile will be poor near the wall where the stretching is small, but be excellent in the region of the tail where the stretching is large. These expectations are confirmed by comparison with the results of the full self-consistent theory even for values of β as small as the order of unity [?]. There are two other, less crucial, assumptions that have been made; that the brush is well characterized only by the one coordinate perpendicular to the grafting surface, and that the polymers are never so strongly stretched that the Gaussian model becomes inapplicable. The first of these requires that the surface coverage satisfy $\sigma a^2 \gg (w/a^3)^{-2/5} N^{-6/5}$, which is the onset of the mushroom regime based on the swelling exponent in good solvent [?]. This requirement is satisfied if w obeys Eq.(10) and if $w/a^3 > 1/N^{1/2}$, which is true for moderately long chains and if one is not too close to the θ-point. The second requirement is that $\hat{z} \ll Na$, which, with the restriction $w/a^3 \ll 1$ is satisfied for coverages $\sigma a^2 < 1$. The Gaussian model is thus applicable whenever mean-field theory is. Thus there is an ample region over which the results of the classical theory should be valid, and it will be of interest to study its application to other polymer systems.

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[2]We note that the present calculation is not a systematic expansion of the partition function, Eq.(1), in powers of $1/\beta$. The accuracy of the classical theory can be estimated from a comparison with a self-consistent field calculation [?].

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FIG. 1. a) Rescaled density profiles $\bar{\phi}$ as a function of the rescaled distance $\bar{z}$ from the grafting surface. Shown are results for $\beta = 0.1$, 1, 10, and 100 (dotted, dash-dotted, dashed, and solid lines, respectively), progressively approaching the asymptotic result (valid for $\beta \to \infty$), shown as a thick dashed line. b) Rescaled end-point distribution $\bar{g}$ as a function of the end-point position $\bar{z}_0$. The results are for the same values of β as in a) and again approach the asymptotic result (thick dashed line). c) End-point stretching $\bar{e}$ as a function of the end-point position $\bar{z}_0$, for the same parameters as in a). Negative values indicates path moves away from grafting surface. d) Difference between maximum $\bar{z}_m(\bar{z}_0)$ and end-point positions $\bar{z}_0$ for the same parameters as in a).