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Polymers Grafted to a Convex Surface

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ABSTRACT: We consider the equilibrium statistics of polymers grafted to the outside of a cylinder in the limit of high molecular weight for small, fixed grafting density. Under melt conditions, we find the exact self-consistent pressure profile, the chain configurations, and the free energy in closed form. These are qualitatively different from the case of concave or flat surfaces: the free chain ends are *excluded* from a zone near the surface, whose thickness grows from zero for a flat surface to a fraction $2/\pi$ of the layer height for a strongly curved cylinder. Despite these differences, the free energy of the convex layer is very well described by the simpler law for the concave layer, analytically continued to convex curvature, for all but the most extreme curvatures. For a cylindrical layer in a marginal solvent, we reduce the conditions for equilibrium to a linear integral equation describing the exclusion zone. For spherical curvature the analogous equation has a quadratic nonlinearity: we discuss the conditions under which this equation is suitable for describing the spherical layer.

I. Introduction

Long polymers grafted to a surface at a fixed areal density σ are strongly perturbed from their ideal random-walk state. As molecular weight increases, the chains must increasingly stretch to avoid overfilling the space they occupy. The scaling properties of this stretched grafted layer were first worked out by de Gennes and Alexander[1,2] and were later elaborated into a self-consistent-field theory by Semenov[3] and by Milner, Cates, and Witten.[4-6] A similar approach has been independently developed by Zhulina and co-workers.[7-14] The central conclusion of the theory is that the free-energy cost to move a monomer from infinity to a height x in the layer is a parabolic function of x. Further features depend on whether the grafted layer is in a neat "melt" state or whether it is immersed in a solvent.

We report here the effect of curving the grafting surface. The case of concave curvature, where the surface curves toward the polymers, was solved by Semenov under melt conditions, and the extension to the solvent case is completely straightforward. The parabolic potential profile is unchanged by the curvature, except for an additive constant, and only the distribution of free chain ends is altered. However, when the surface is convex, curving away from the chains, their state is qualitatively altered. The parabolic potential profile no longer gives a self-consistent solution: in such a potential there is no physical (i.e., positive) distribution of free ends that allows the monomers to fill space uniformly. Semenov[3] pointed this out for the melt case and noted that to regain self-consistency, free ends should be excluded from a zone near the surface.

In this paper we develop a quantitative theory of this exclusion zone and its consequences for the chain stretching. In this regime the simple picture for flat surfaces is lost; the "equal-time" constraint on the potential profile now only holds outside the exclusion zone. In its place we derive a pair of integral equations coupling the potential in the exclusion zone to the end distribution in the end-containing zone beyond. For the case of cylindrical curvature, we find that this problem can be reduced to a single linear integral equation. For the case of a melt, this may be further transformed to a two-dimensional electrostatics problem and thereby solved. Using this solution, we find that the exclusion zone is exponentially small for weak curvatures and that it grows to a fraction $2/\pi$ of the layer thickness h in the limit of strong cylindrical curvature. We derive the free energy needed to curve the layer and contrast this with the case of concave curvature. For all but the most extreme curvatures, we find that this free energy is extremely well approximated by analytically continuing the simple results for concave curvature to the convex regime.

The properties of the energy of a convex layer have important consequences for polymer and surfactant systems. In the surfactant case the present theory describes approximately the interfaces of oil-continuous microemulsions. The bending energy of these ubiquitous interfaces is thought to play[15] a crucial role in the phase stability of microemulsions. Surfactants and copolymers at high concentration organize themselves into a variety of periodic structures,[16,17] all of which have random coils end-attached to convex surfaces. The present theory is a step toward understanding how the system chooses among these structures and how they respond to deformation.[18,19] Finally, colloidal particles in solution are commonly stabilized by a layer of grafted polymers.[20] The present theory gives insight into how the convexity of these layers affects their stored energy and their polymer concentration profile. It is also applicable to comb and star polymers.

The formalism for the cylindrical melt is readily modified to take into account the immersion of the layer in a solvent. The integral equation linking the end distribution to the exclusion-zone potential is quite similar to that obtained in the case of the melt but cannot, however, be readily transformed into an electrostatics problem. For spherical curvature, the integral equation determining the self-consistent potential is no longer linear but is quadratic, with slightly different kernels in the melt and solvent cases. We exhibit all of these integral equations but defer analysis of them to future publications.

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II. Conditions for Self-Consistency

Identical flexible polymers are grafted to the outside of a cylinder (or sphere) with radius of curvature R. The surface contains σ chains per unit area. In the absence of solvent, the grafted chains form an essentially incompressible melt, so that the length of each polymer may be measured by the volume V it displaces in the melt state. We imagine that the grafted layer is immersed in a melt of high molecular weight homopolymer. Under the conditions of strong stretching (to be made more precise in section V), these external chains penetrate arbitrarily little into the grafted layer,[19] so that we may treat the layer in isolation. Under these conditions, the height h_0 of the layer on a flat surface is $V\sigma$.

To extend a section of chain of volume ΔV costs an elastic free energy $K\Delta V$, where K is proportional to the extension squared $(\Delta x)^2$:

$$K = \frac{1}{2}(kT)a[\Delta x/\Delta V]^2 \tag{1}$$

Here the "packing length" coefficient, a, depends on the chemical makeup of the chain and is typically on the order of 10 Å.[18] In the ungrafted melt state, this section would have a mean-squared end-to-end distance of $3\Delta V/a$, and its mean elastic energy would be $3kT/2$. We shall express all energies henceforth in units of kT.

The section ΔV contains a second form of (free) energy, owing to its interactions with other chains: work is required to insert such a section into the grafted layer at height x. Inserting the section must displace the other chains, increase the height of the layer, and thereby store additional elastic energy. This work is proportional to the volume displaced and is of the form $p(x)\ \Delta V$. Thus there is a pressure $p(x)$ in the layer.[21,22] It is this pressure that pushes a given chain out to the required extended state.

We may label a position along the chain by the chain length, υ, between that position and the free end (in volume units). Then each chain configuration may be expressed by the function $\vec{r}(\upsilon)$ relating the spatial position $\vec{r}$ of a point υ along the chain. In the limit of long chains, $V\sigma^2 a \gg 1$, the chains extend over distances of order h_0, which are much greater than their ideal radius $(3V/a)^{1/2}$. Thus a typical chain ending at x_0 fluctuates only narrowly about that path $x(\upsilon)$, which minimizes its total free energy S

$$S[x(\upsilon)] = \int_0^V \mathrm{d}\upsilon \left[\frac{1}{2}a\left(\frac{\mathrm{d}x}{\mathrm{d}\upsilon}\right)^2 + p(x(\upsilon))\right] \tag{2}$$

subject to the constraints that $x(0) = x_0$ and $x(V) = 0$.[4]

The variational problem of finding the optimum path, $x(\upsilon)$, is equivalent to the problem of determining the trajectory of a classical particle subject to Newton's laws of motion. Indeed, the functional S is simply the classical action[23] of a particle of mass a moving in a potential $-p(x)$, with the arc length, υ, playing the role of time. The path $x(\upsilon)$ that minimizes the polymer energy S is the trajectory of least action. The Euler–Lagrange equation that results is Newton's second law of motion

$$a\ \mathrm{d}^2x/\mathrm{d}\upsilon^2 = \mathrm{d}p/\mathrm{d}x \tag{3}$$

with the boundary conditions $x(0) = x_0$ and $x(V) = 0$. The path $x(\upsilon)$ of the chain is thus the trajectory of a Newtonian particle released from height x_0 and arriving at the grafting surface at "time" V. We review here the implications of (3) to show the new features that appear with a curved surface.

To find the state of the chains in the layer, we must determine the set of free-end positions $\{x_0\}$ and the pressure profile $p(x)$. These must be chosen to assure that (a) each chain is in mechanical equilibrium and (b) the chains have a local density everywhere that is compatible with their melt state. A profile $p(x)$ and set of end positions $\{x_0\}$ that satisfy these conditions are *self-consistent*.

The equilibrium condition (a) sets a further constraint on the Newton's law trajectory. In general, a trajectory satisfying (3) will need a nonzero initial "velocity" $\mathrm{d}x/\mathrm{d}\upsilon|_{x_0}$, in order to reach the surface in a "time" V. This velocity represents a chain extension and hence a tension in the chain at its end. In equilibrium there can be no such tension: the initial "velocity" must thus be zero. This sets a condition on the potential $p(x)$ that may be formulated as thus: the potential $p(x)$ must be such that for any height x containing free ends, a Newtonian particle released from *rest* reaches the surface in a fixed "time" V. The profile $p(x)$ is an "equal time potential", in any region where free ends are found.

To express the equal-time condition quantitively, we write the "time" V as a sum of time increments at each height x:

$$V = \int_{x_0}^0 \mathrm{d}x\ (\mathrm{d}x/\mathrm{d}\upsilon)^{-1} \tag{4}$$

The "velocity" $\mathrm{d}x/\mathrm{d}\upsilon$ is related to $p(x)$ by conservation of energy: $(a/2)(\mathrm{d}x/\mathrm{d}\upsilon)^2 - p(x) = -p(x_0)$. Thus

$$V = -\int_{x_0}^0 \mathrm{d}x\ (a/2)^{1/2}[p(x) - p(x_0)]^{-1/2} \tag{5}$$

The negative root reflects the fact that the motion is that of a particle falling toward the grafting surface.

The equation may be simplified by labeling the position by its pressure p rather than by x[24]

$$V(p_0) = -(a/2)^{1/2}\int_{p_0}^P \mathrm{d}p\ \frac{\mathrm{d}x}{\mathrm{d}p}[p - p_0]^{-1/2} \tag{6}$$

where p_0 is the pressure at the free end and P is that at the surface. This convolution integral equation may be readily inverted[25] to give $\mathrm{d}x/\mathrm{d}p$

$$\frac{\mathrm{d}x}{\mathrm{d}p}\Big|_{p_0} = \left(\frac{2}{\pi^2 a}\right)^{1/2}\int_{p_0}^P \mathrm{d}p\ \frac{\mathrm{d}V}{\mathrm{d}p}[p - p_0]^{-1/2} \tag{7}$$

provided $V = 0$ at $p = P$. For a flat (or concave) surface[4] $V(p)$ is a constant, V for all p away from the surface. Thus $\mathrm{d}V/\mathrm{d}p$ is simply a δ function at $p = P$, and $\mathrm{d}x/\mathrm{d}p = -V(2/\pi^2 a)^{1/2}[P - p]^{-1/2}$. This is the equation for the parabolic $p(x)$ of refs 4 and 5.

A serious problem arises if one presumes a potential that satisfies the equal-time constraint throughout a *convex* layer. Below, we will find that this parabolic potential proves incompatible with the requirement of uniform density: it forces the density of free ends to become *negative* near the grafting surface[3,6] in order to maintain the monomer density at its constant melt value.

For a convex surface, we accordingly allow an exclusion zone between the surface pressure P and some intermediate height at pressure Q between zero and P. The equal-time condition $\mathrm{d}V/\mathrm{d}p = 0$ must hold only where there are free ends, i.e., for $p < Q$. For $Q < p < P$, $\mathrm{d}V/\mathrm{d}p$ is an unknown function to be determined. Given this function, the profile $\mathrm{d}x/\mathrm{d}p$ is determined by

$$\frac{\mathrm{d}x}{\mathrm{d}p}\Big|_{p_0} = \left(\frac{2}{\pi^2 a}\right)^{1/2}\int_{\max(p_0,Q)}^P \mathrm{d}p\ \frac{\mathrm{d}V}{\mathrm{d}p}[p - p_0]^{-1/2} \tag{8}$$

Though we have discussed this equation in the context of a melt, it applies equally well in the presence of solvent. The "pressure" $p(x)$ must retain its definition as the work to insert a volume ΔV of chain at x and thus becomes a chemical potential rather than a pressure. We discuss this in more detail below in section IV.

We now turn to condition (b) for equation-of-state equilibrium of the melt or solution. To state this condition succinctly, we define the distribution of end positions $\{x_0\}$ more precisely. Of the σ chains in a unit of area we define $\sigma(p_0)$ to be the number ending *beyond* the pressure p_0. Thus for the extremity of the layer, where, where $p = 0$, $\sigma(0) = 0$. For the surface, where $p = P$, $\sigma(P) = \sigma$. Moreover, if there is an exclusion zone between Q and P, $\sigma(p) = \sigma$ throughout this zone, since no further ends are to be found there.

We may now state the condition of uniform monomer density in terms of $\sigma(p)$. At height x and pressure p, the total volume of the chains occupying a slice of thickness $\mathrm{d}x$ of height must be the volume of that slice. This volume corresponding to an area A of the grafting surface is $A[1 + x/R]\,\mathrm{d}x$ for a cylinder and $A[1 + x/R]^2\,\mathrm{d}x$ for a sphere. The chains contributing to this volume must all end at heights greater than x and hence at pressures lower than p. Therefore, for an area A of a cylindrical grafting surface

$$A[1 + x/R]\,\mathrm{d}x = \sum_\alpha (\mathrm{d}\upsilon/\mathrm{d}x)_\alpha\,\mathrm{d}x \qquad (9)$$

where the sum α runs over all chains extending beyond height x grafted to the area A. The left-hand side of (9) is altered in the presence of solvent since there not all of the available volume is occupied by chains, as discussed in section IV.

In terms of the distribution $\sigma(p)$, eq 9 can be written as

$$[1 + x/R] = -\int_0^p \mathrm{d}p_0\, \frac{\mathrm{d}\sigma}{\mathrm{d}p}\Big|_{p_0} \frac{\mathrm{d}\upsilon}{\mathrm{d}x}\Big|_{p_0\to p} \qquad (10)$$

where the $\mathrm{d}\upsilon/\mathrm{d}x$ in the integrand is for a chain segment at pressure p for which the free end is at pressure p_0. This $\mathrm{d}\upsilon/\mathrm{d}x$ is simply the inverse velocity used in (5). The resulting convolution integral is nearly identical to (5) above. It may be inverted in the same way to yield an expression for the unknown $\mathrm{d}\sigma/\mathrm{d}p$:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}p} = \left(\frac{2}{\pi^2 a}\right)^{1/2} \int_0^p \mathrm{d}p_0\, \frac{\mathrm{d}[1 + x/R]}{\mathrm{d}p}\Big|_{p_0} (p - p_0)^{-1/2} \qquad (11)$$

As in (8), this inverse carries the formal condition that the [ ] factor be zero at $p = 0$, and so for the melt, d[ ]/dp must include a δ function of amplitude $1 + h/R$ at $p = 0$.

In a convex layer, this condition cannot be satisfied if the pressure has the parabolic form present in a flat or concave layer. With the parabolic potential, the d[ ]/dp factor varies as $-(P-p)^{-1/2}$. This gives rise to a contribution to $\mathrm{d}\sigma/\mathrm{d}p$ of the form $R^{-1}\log(P - p)$, which dominates as $p \to P$. This forces $\mathrm{d}\sigma/\mathrm{d}p$ to become negative near the grafting surface for any convex surface (i.e., $0 < R < \infty$). It is to avoid this unphysical state of affairs that we are obliged to consider the exclusion zone. We note that the singularity in d[ ]/dp is present with or without solvent, so that an exclusion zone is anticipated in either case. For concave surface ($R < 0$) the singularity is of the opposite sign, and this problem does not arise.

For points $p < Q$, beyond the exclusion zone, (11) determines $\mathrm{d}\sigma/\mathrm{d}p$ in terms of the phase-space factor [ ]. For points $p > Q$ within the exclusion zone, $\mathrm{d}\sigma/\mathrm{d}p$ must be zero, and the equation imposes a condition on how the phase-space factor must vary with pressure. Equations 8 and 11 contain the conditions for equilibrium of the grafted layer. We show below that these may be reduced to an equation for a single unknown function, namely the "transit-time profile" $\mathrm{d}V/\mathrm{d}p$ in the exclusion zone. We shall treat this reduction case by case.

III. Melt Grafted to a Cylindrical Surface

In this case the unknown derivative of the phase-space factor in (11) may be readily expressed in terms of $\mathrm{d}x/\mathrm{d}p$

$$\frac{\mathrm{d}[1 + x/R]}{\mathrm{d}p} = R^{-1}\frac{\mathrm{d}x}{\mathrm{d}p} + [1 + h/R]\,\delta(p) \qquad (12)$$

where $\mathrm{d}x/\mathrm{d}p$ is given by (8). Using (12) and (8) in (11), we obtain

$$\frac{\pi a R}{4}\frac{\mathrm{d}\sigma}{\mathrm{d}p} = \frac{1}{2\pi}\int_0^p \mathrm{d}p_0 \int_{\max(p_0,Q)}^P \mathrm{d}p'\, \frac{\mathrm{d}V}{\mathrm{d}p}\Big|_{p'} (p' - p_0)^{-1/2}(p - p_0)^{-1/2} + \left(\frac{a}{8}\right)^{1/2}[R + h]p^{-1/2} \qquad (13)$$

Performing the p_0 integration, the first term on the right-hand side of (13) has the form

$$\frac{1}{2\pi}\int_Q^P \mathrm{d}p'\, K(p,p')\, \frac{\mathrm{d}V}{\mathrm{d}p}\Big|_{p'} \qquad (14)$$

where

$$K(p,p') = \log\frac{\sqrt{p} + \sqrt{p'}}{|\sqrt{p} - \sqrt{p'}|}$$

This "exclusion-zone" equation is a functional constraint on $\mathrm{d}V/\mathrm{d}p$ for each point p in the exclusion zone, where $\mathrm{d}\sigma/\mathrm{d}p = 0$. This is in principle sufficient information to determine $\mathrm{d}V/\mathrm{d}p$ uniquely over that zone. This information is in turn sufficient to determine the pressure profile $\mathrm{d}x/\mathrm{d}p$ everywhere from (8) and, from it, all other unknown quantities.

(a) Electrostatic Analogy. To reduce the equation further, we note that the logarithmic singularity in the kernel K is reminiscent of the Green's function for the Laplace equation in two dimensions familiar from electrostatics. To discuss this resemblance, we define a position variable $u \equiv p^{1/2}$. Equation 13 then becomes, for $p \leq Q$

$$0 = \left(\frac{a}{8}\right)^{1/2}[R + h]u^{-1} + \frac{1}{2\pi}\int_{Q^2}^{P^2} \mathrm{d}u'\, [\log(u + u') - \log|u - u'|]\,\frac{\mathrm{d}V}{\mathrm{d}u'} \qquad (15)$$

The first logarithm may be written $\log|u - (-u')|$; thus by using the integration variable $-u'$ for the first logarithm, we may rewrite (15) as

$$0 = -\frac{1}{2\pi}\int_{-P^2}^{-Q^2} \mathrm{d}u'\,\log|u - u'|\,\frac{\mathrm{d}V}{\mathrm{d}u'} + \left(\frac{a}{8}\right)^{1/2}[R + h]u^{-1} - \frac{1}{2\pi}\int_{Q^2}^{P^2} \mathrm{d}u'\,\log|u - u'|\,\frac{\mathrm{d}V}{\mathrm{d}u'} \qquad (16)$$

for $Q^2 < u < P^2$. Here we have defined $\mathrm{d}V/\mathrm{d}u$ for negative u by requiring it to be odd in u.

This may be interpreted as an equation for an electrostatic potential $(\pi a/4)R\,\mathrm{d}\sigma/\mathrm{d}p$ in two dimensions, in the presence of a dipole source of strength $(a/8)^{1/2}[R + h]$ at the origin and a pair of line charges of density $\mathrm{d}V/\mathrm{d}u$ lying on the x axis between $u = Q^2$ and $u = P^2$ and between $u = -P^2$ and $u = -Q^2$. The exclusion-zone equation (16) indicates that the potential is zero on the charge distribution on the positive side and must also be zero on the negative side as well by symmetry. Hence these lines of charge appear to be grounded conductors. The potential along the y axis also vanishes by symmetry: we may regard the y axis as a grounded conductor and remove the image charges on the negative x axis. The dipole source becomes a point charge next to the origin.

We may now readily carry this electrostatic interpretation back to our original pressure variable p, by simply remapping the complex variable u into $p \equiv u^2$. Accordingly, we imagine the pressure as a two-dimensional variable. The vertical conductor in the u plane becomes the negative p axis, while the horizontal segment has the same shape in the p plane. This segment is now the exclusion zone: the origin is the extremity of the grafted layer, and the x axis between the origin and the exclusion zone is the end-containing region. We note that, although this electrostatic representation is inherently two-dimensional, only the x axis of this p plane has an obvious physical interpretation in our problem.

The exclusion-zone equation becomes

$$0 = \frac{\pi a R}{4}\frac{\mathrm{d}\sigma}{\mathrm{d}p} = -\int_{-\infty}^{0}\frac{\mathrm{d}p'}{2\pi}\log|p - p'|\frac{\mathrm{d}V}{\mathrm{d}p'} - \int_{Q}^{P}\frac{\mathrm{d}p'}{2\pi}\log|p - p'|\frac{\mathrm{d}V}{\mathrm{d}p'} \quad (17)$$

for $p < 0$ and $Q < p < P$. The explicit point dipole of (16) becomes the condition that the potential must diverge as $(a/8)^{1/2}[R + h]p^{-1/2}$ as one approaches the origin along the x axis.

Solving this electrostatic boundary value problem gives the complete solution of the grafted polymer layer. In the electrostatic problem, one is given the strength of the source $(a/8)^{1/2}(R + h)$ and the placement of the conductor from $x = Q$ to $x = P$. From this information one may determine the induced charge density, $\mathrm{d}V/\mathrm{d}p$, and the electrostatic potential, $(\pi a R/4)\,\mathrm{d}\sigma/\mathrm{d}p$. The total charge, $\int \mathrm{d}p\,\mathrm{d}V/\mathrm{d}p$, is evidently the molecular volume. Likewise, the integral of the potential from 0 to Q is $\pi a R\sigma/4$ and thus gives the coverage. R itself is determined by the outer radius, $R + h$, the chain length V and the coverage, σ, by the requirement of space filling. The induced charge density and potential are evidently positive and thus give physically meaningful end densities and chain lengths.

(b) Scaling Properties. Much of the dependence of the quantities P and Q on the independent variables V, σ, and R is determined by scaling properties. By examination of (17), we note that from any valid solution we may obtain another by scaling the molecular weight V, the radius R, and outer radius, $[R + h]$, by the same factor. The coverage, σ, and all pressures are left unchanged by this scale transformation; correspondingly the surface pressure, P, and the zone-boundary pressure, Q, are unchanged. This rescaling has no effect on the integral equation (17) and its boundary condition. The ratio h/R, which is fixed solely by the space-filling requirement

$$[R + h]^2 - R^2 = 2Rh_0 = 2R\sigma V \quad (18)$$

is also unaltered by this scaling.

A second scaling symmetry in the equation is demonstrated by scaling all pressures by a factor λ^2, without changing the chain length V. This changes the charge density, $\mathrm{d}V/\mathrm{d}p$, by a factor λ^{-2} but leaves the integrals in (17) invariant. In order for the point source term to remain invariant, the outer radius, $[R + h]$, must be scaled by a factor λ. Finally, the potential $(\pi a R/4)\,\mathrm{d}\sigma/\mathrm{d}p$ must not change, and this may be achieved by scaling the total coverage, σ, and the radius, R, each by a factor λ, to compensate for the scaling of p. To summarize, scaling lengths R, h, and coverage σ by the same factor gives an equivalent system of the same chain length, with pressure increased everywhere by the square of this factor. Of the three independent variables R, h, and V, two may be removed by these scaling symmetries, leaving a single nontrivial variable: the ratio h/R.

(c) Exact Solution of Exclusion-Zone Equation. A standard method from the theory of analytic functions[26] exists to find the potential in the p plane subject to the previously described boundary conditions and hence to solve the exclusion-zone equation. We shall regard the potential $(\pi a R/4)\,\mathrm{d}\sigma/\mathrm{d}p$ as the real part of a complex function in the complex p plane. This potential must satisfy the following conditions: (a) it must satisfy the Laplace equation except on the conductors; thus it must be analytic in the complex p plane except on the negative real axis and in the exclusion zone; (b) the real part of the potential must vanish on the conductors; therefore, the complex potential function must be purely imaginary on the negative real axis and in the exclusion zone; (c) near the point source at the origin, the potential must diverge as $(a/8)^{1/2}[R + h]p^{-1/2}$; (d) the potential must vanish at infinity.

A function with these properties may be written as

$$\frac{\pi a R}{4}\frac{\mathrm{d}\sigma}{\mathrm{d}p} = \left(\frac{a}{32}\right)^{1/2}[R + h]\int_{p}^{\infty}\frac{\mathrm{d}p'}{p'}\frac{1 - cp'}{(p')^{1/2}} \times \left[\frac{PQ}{(Q - p')(P - p')}\right]^{1/2} \quad (19)$$

The constant c is determined by the requirement that the integral vanishes at $p = P$. Once c is set, the potential vanishes as required in the exclusion zone due to the integrand being purely imaginary for $Q \leq p \leq P$. The potential also vanishes on the negative real axis, since this integrand is also imaginary and since the potential vanishes at infinity. Condition c may be verified by differentiating (19) near the origin.

The charge density, $\mathrm{d}V/\mathrm{d}p$, is the electric field just above the conductor, i.e., the real part of the derivative of the potential in the imaginary direction. This is simply twice the imaginary part of the integrand of (19):

$$-\frac{\mathrm{d}V}{\mathrm{d}p} = \left(\frac{a}{8}\right)^{1/2}[R + h]\frac{1 - cp}{p^{3/2}}\left[\frac{PQ}{(p - Q)(P - p)}\right]^{1/2} \quad (20)$$

(d) Weak-Curvature Limit. We now discuss the two limiting cases of curvature. In the weakly curved limit, $h/R \ll 1$, the grafted layer is almost indistinguishable from a flat layer. The zone-boundary pressure, Q, must approach P, and so the exclusion-zone conductor in the electrostatic p plane shrinks nearly to a point. The charge density, $\mathrm{d}V/\mathrm{d}p$, arises from a nearly uniform field and becomes symmetrical: $\mathrm{d}V/\mathrm{d}p = -(V/\pi)[(p - Q)(P - p)]^{-1/2}$. The exclusion-zone equation may be used to link the zone-boundary pressure to the layer curvature and surface coverage. It is convenient to use the equation as expressed in (15), for in this limit, only the short-range behavior of the kernel K is important. For small $p - p'$, the kernel is dominated by the logarithmic divergence $K(p,p') = \log|4p/(p - p')| + \mathcal{O}(p - p')$, and insertion of this into the end-zone equation (13) evaluated at $p = P$ leads to

$$\left(\frac{a}{8}\right)^{1/2}\frac{R + h}{\sqrt{P}} = \frac{1}{2\pi}\int_{Q}^{P}\mathrm{d}p'\log[4P/(P - p')]\left[-\frac{\mathrm{d}V}{\mathrm{d}p}\right]_{p'} = \frac{V}{2\pi}\log\frac{4P}{(P - Q)} \quad (21)$$

where (small) corrections of order $P - Q$ are ignored.

In the weakly curved limit we may replace h and P by their values in the flat layer, $h \approx h_0 = \sigma V$ and $P \approx P_0 = \pi^2\sigma^2 a/8$. Equation 21 thus becomes

$$2(1 + R/h_0) = \log[4P_0/(P - Q)] + \mathcal{O}(e^{-4R/h_0})$$

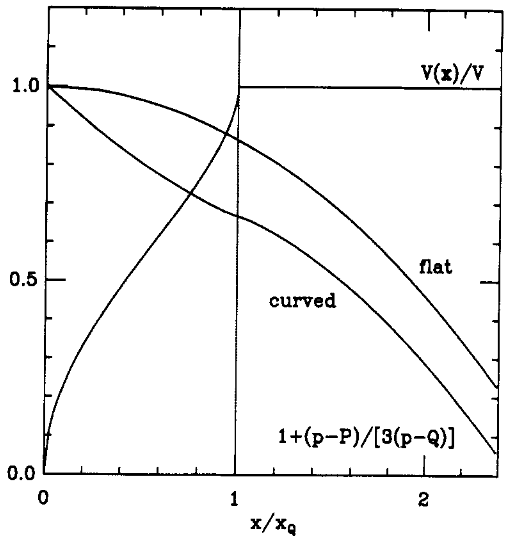

Figure 1. Pressure and transit time for the nearly flat grafted layer. $1 + (p - P)/[3(P - Q)]$ for the curved, and corresponding flat, layers are shown, along with the transit time $V(x)/V$. Distance is given in units of the exclusion-zone height, x_Q. The curved layer pressure shows a logarithmic singularity in inverse slope at the edge of the exclusion zone, while the flat layer is smooth. The two pressures asymptotically agree above the exclusion zone. The transit time is constant above the exclusion zone and drops to zero as one approaches the grafting surface.

or

$$P - Q = 4P_0 \exp(-2R/h_0) + \mathcal{O}(e^{-4R/h_0}) \qquad (22)$$

leading to the conclusion that the pressure drop across the exclusion zone is exponentially small in the radius of curvature of the layer. Equation 8 can be directly integrated to find the exclusion-zone height, x_Q:

$$x_Q = V\left(\frac{2}{\pi^2 a}\right)^{1/2} \int_Q^P \mathrm{d}p'\,(p' - Q)^{-1/2} = 2h_0 \exp(-R/h_0) + \mathcal{O}(e^{-2R/h_0}) \qquad (23)$$

The exclusion-zone height is also exponentially small in the ratio of the uncurved layer height to the cylinder radius.

The pressure profile can also be obtained from (8). The term $\mathrm{d}V/\mathrm{d}p$ in the integrand diverges logarithmically when $p = Q$, and therefore all derivatives of p with respect to x vanish at the exclusion-zone boundary. In Figure 1 we display $p(x)$ in the vicinity of the exclusion zone in the limit of very slight curvature, along with the corresponding pressure profile for the flat layer. It is evident that the slightly curved and flat profiles become the same far above the (very small) exclusion zone. We also display the transit time, $V(x)$, as a function of height: it is the molecular volume V for $x > x_Q$, but as the grafting surface is approached, in the exclusion zone, it drops to zero. In Figure 2 we plot the trajectory, $x(\upsilon)$, of the chain that starts from the edge of the exclusion zone at x_Q for the nearly flat layer, along with the trajectory of the chain that starts from the top of the layer (or equivalently, the trajectory of any chain in the flat layer).

(e) Strong-Curvature Limit. In the opposite limit, the inner edge of the exclusion zone approaches the origin, and $Q/P \rightarrow 0$. In this limit, with fixed source strength $R + h$, the induced charge $V \rightarrow \infty$. If the converage σ is held fixed, the space-filling condition (18) implies that $R \approx 1/V \rightarrow 0$ relative to $R + h$. Thus $R/h \rightarrow 0$, indicating that this is the strongly curved limit. To complete the solution, we note that the condition for the constant c in (19) is in this limit

$$0 = \int_\infty^P \frac{\mathrm{d}p'}{p'} \frac{1 - cp'}{(p')^{1/2}} \left[\frac{1}{(p')(p' - P)}\right]^{1/2} \qquad (24)$$

which is solved by $c = (2P)^{-1}$. For very large h_0/R, the thickness of the layer is set by the space-filling condition (19) to be $h/R = (2V\sigma/R)^{1/2}$.

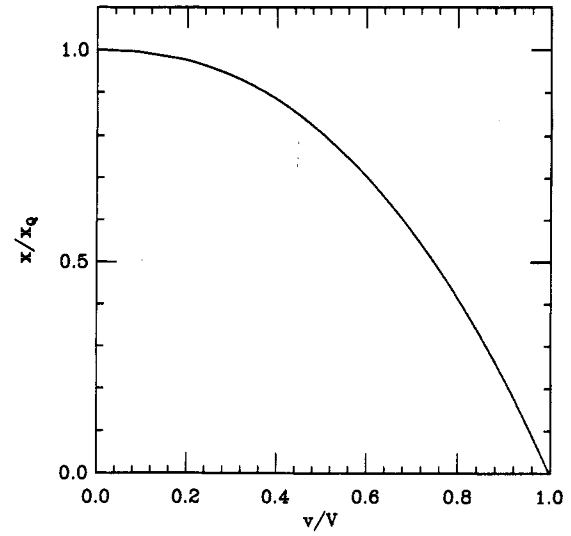

Figure 2. Trajectory of the chain with the free end at the edge of the exclusion zone. Distance in units of x_Q drops to zero as the time υ increases from 0 to V. Note the nearly parabolic shape of the trajectory.

For the strongly curved limit, the potential $(\pi a R/4)\,\mathrm{d}\sigma/\mathrm{d}p$ may be integrated to find the coverage σ in terms of the surface pressure P:

$$\sigma = \int_0^Q \mathrm{d}p \frac{\mathrm{d}\sigma}{\mathrm{d}p} = (2P/a)^{1/2} \qquad (25)$$

Evidently, P is reduced by the purely numerical factor $4/\pi^2$ relative to the flat layer but remains independent of the overall height, h, and chain length, V. The boundary pressure Q can be obtained from substitution of (20) into the sum rule $V = \int_Q^P \mathrm{d}p\,\mathrm{d}V/\mathrm{d}p$, which allows us to conclude that $Q = a\sigma R/V$, which is smaller than P by a factor of order R^2/h^2, in agreement with the preceeding conclusion that $Q/P \rightarrow 0$ as the curvature is increased.

The exclusion zone height, x_Q, may be found to be

$$x_Q = -\int_Q^P \mathrm{d}p \frac{\mathrm{d}x}{\mathrm{d}p} = -\left(\frac{2}{\pi^2 a}\right)^{1/2} \int_Q^P \mathrm{d}p \int_p^P \mathrm{d}p' \frac{\mathrm{d}V}{\mathrm{d}p'} (p' - p)^{-1/2} \qquad (26)$$

Power counting (20) tells us that $\mathrm{d}V/\mathrm{d}p$ is of order $a^{1/2}P^{-3/2}h$ for strong curvature; thus from dimensional analysis of (26), we expect that x_Q will be of order h, and, in fact, (26) can be integrated to show that, as $h/R \rightarrow \infty$ and hence as $Q/P \rightarrow 0$, $x_Q \rightarrow (2/\pi)h$.

In Figure 3 we display the pressure profile in the limit of strong curvature. Figure 3a shows the global pressure profile, with pressure in units of Q, the pressure at the top of the exclusion zone. However, P cannot be shown on this plot because $Q/P = 0$ in this limit. Figure 3b shows the pressure profile in units of P, near the bottom of the layer. In Figure 3b, Q and x_Q cannot appear, since the scale for variations of pressure of order P is a distance R, which is zero on the scale of the exclusion-zone height.

(f) Intermediate Curvature. For intermediate curvatures, all results can be expressed in terms of the elliptic integrals

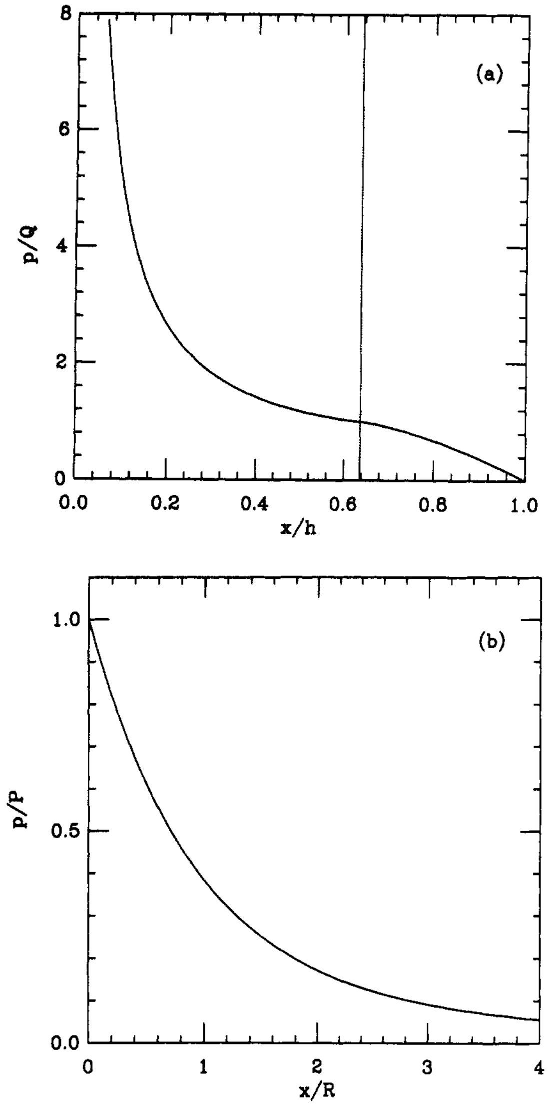

Figure 3. Pressure as a function of height in the strongly curved limit. (a) Pressure, in units of the pressure at the top of the exclusion zone Q, vs height in units of the total layer height, h. The top of the exclusion zone is thus at $2/\pi$ on this graph. (b) Pressure at the bottom of the exclusion zone: pressure is in units of P, and height is in units of the radius of curvature, R. On the scale of (b), $Q = 0$ and $h = \infty$.

$$F(\phi,k) = \int_0^{\phi} \mathrm{d}\theta\,(1 - k^2 \sin^2\theta)^{-1/2}$$
$$E(\phi,k) = \int_0^{\phi} \mathrm{d}\theta\,(1 - k^2 \sin^2\theta)^{1/2} \tag{27}$$

The normalization constant, c, is given by

$$cQ = 1 - \frac{E(\pi/2, [Q/P]^{1/2})}{F(\pi/2, [Q/P]^{1/2})} \tag{28}$$

Although c appears to be of order Q^{-1} for strong curvatures, it is actually of order P^{-1} due to the fact that $1 - E(\pi/2,k)/F(\pi/2,k) \approx k^2$ for small k. The layer height h can be directly computed via the integration of (8):

$$h = -\int_0^P \mathrm{d}p\,\frac{\mathrm{d}x}{\mathrm{d}p} = [R + h][1 - c(PQ)^{1/2}] \tag{29}$$

This relation allows the known layer geometry to be directly related to the pressures P and Q.

Since the charge density, $\mathrm{d}V/\mathrm{d}p$, must always diverge as $(p - Q)^{-1/2}$, the derivative $\mathrm{d}x/\mathrm{d}p$ in (8) always diverges logarithmically at the exclusion-zone boundary, as can be seen by the general result for the cylindrical melt

$$-\frac{\mathrm{d}x}{\mathrm{d}p} = \frac{R+h}{\pi[pPQ(t-Q)]^{1/2}}\left[(t - cPQ)F\left(\frac{\pi}{2},\left[\frac{b-Q}{t-Q}\right]^{1/2}\right) - (t-Q)E\left(\frac{\pi}{2},\left[\frac{b-Q}{t-Q}\right]^{1/2}\right)\right] \tag{30}$$

where $t = \max\{P,PQ/p\}$ and $b = \min\{P,PQ/p\}$. The divergence is due to the behavior $F(\phi,k) \approx \log(4/(1 - k^2)^{1/2})$ for $k \to 1$. Thus P and Q set both the total layer height (19) and the excluded-zone height:

$$x_Q = -\int_Q^P \mathrm{d}p\,\frac{\mathrm{d}x}{\mathrm{d}p} = \frac{2[R+h]}{\pi}[(1 - Q/P)^{1/2} - c(PQ)^{1/2}\tan^{-1}(P/Q - 1)^{1/2}] \tag{31}$$

The coverage $\sigma = \int_0^Q \mathrm{d}p\,\mathrm{d}\sigma/\mathrm{d}p$ has the form

$$\sigma = \left[\frac{2}{\pi^2 aQ}\right]^{1/2}\left[1 + \frac{h}{R}\right]\int_0^Q \mathrm{d}p\left[(1 - Qc)F(\alpha,(Q/P)^{1/2}) - E(\alpha,(Q/P)^{1/2}) + \left[\frac{P}{p}\left(\frac{Q/p - 1}{1 - p/P}\right)\right]^{1/2}\right] = \left[\frac{2Q}{\pi^2 a}\right]^{1/2}\left[1 + \frac{h}{R}\right][(1 - cP)F(\pi/2,(Q/P)^{1/2}) + cPE(\pi/2, (Q/P)^{1/2})] \tag{32}$$

where $\alpha = \tan^{-1}([Q/p - 1]/[1 - Q/P])^{1/2}$. Clearly $\mathrm{d}\sigma/\mathrm{d}p$ vanishes at the edge of the exclusion zone ($p = Q$), increases with decreasing pressure (as x increases), and is nonsingular except for the square-root divergence at the top of the layer ($p = 0$) encountered in the study of the flat melt.[3,4] The total chain length $V = \int_Q^P \mathrm{d}p\,\mathrm{d}V/\mathrm{d}p$ is

$$V = \left(\frac{\pi^2 a}{8Q}\right)^{1/2}\frac{R+h}{F(\pi/2,(Q/P)^{1/2})} \tag{33}$$

To obtain this result, (28) and the identity[27]

$$\frac{\pi}{2} = E(\pi/2,k')\,F(\pi/2,k) + E(\pi/2,k)\,F(\pi/2,k') - F(\pi/2,k)\,F(\pi/2,k')$$

where $k' = (1 - k^2)^{1/2}$, are needed. The formulas (21), (32), and (33) can easily be shown to satisfy the packing constraint (18).

Figure 4 indicates how the pressures P and Q and the zone height x_Q vary with curvature. $P/(\sigma^2 a)$ changes from $1/2$ to $\pi^2/8$ as the radius of curvature R is increased from 0 to ∞, while Q changes from zero (for $R = 0$) to P (for large R). The exclusion-zone height drops smoothly to zero from its value of $2h/\pi$ at $R = 0$.

One can compare this exact solution of the integral equation with the result of the "Alexander–de Gennes" calculation extended to the grafted cylindrical melt. This approximation consists of the assumption of a δ-function end distribution ($\mathrm{d}\sigma/\mathrm{d}x = \sigma\delta[x-h]$). Insertion of this into (10) immediately gives us the stretch $\mathrm{d}x/\mathrm{d}v$. The Alexander–de Gennes approach presumes nonzero stretch at the top of the layer; namely, $\mathrm{d}x/\mathrm{d}v|_{x=h} = \sigma R/(R + h)$. This nonzero "initial velocity" can only be caused by a discontinuity in the "potential", i.e., the pressure, assuming that for polymers outside the layer, there is no stretch and zero pressure. In fact, the pressure profile of the general case is simply

$$p = \frac{1}{2}a\sigma^2 R^2[(R + h)^{-2} + (R + x)^{-2}]\Theta(h-x) \tag{34}$$

where $\Theta(x)$ is the unit step function. We note that this approximation leads to a pressure at the grafting surface that is $P = a\sigma^2$ for the flat case ($R = \infty$) and $P = a\sigma^2/2$ for

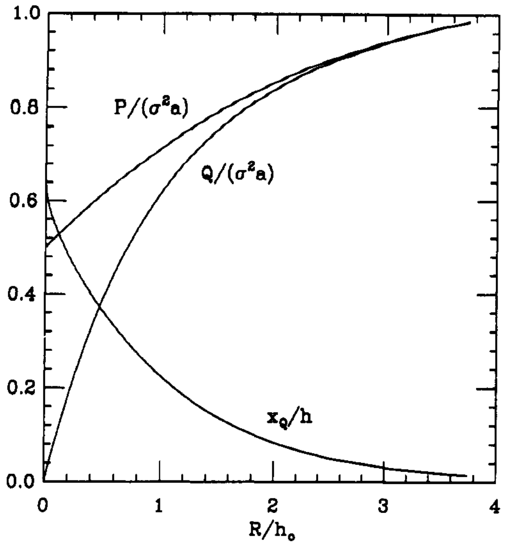

Figure 4. Results for exclusion-zone heights and pressures as a function of curvature. Curvature is given in terms of R/h_0, while σ and V are considered fixed. The exclusion-zone height drops from $2/\pi$ to 0 as the radius of curvature is increased from zero, while the grafting surface pressure P changes from 1/2 to $\pi^2/8$, in units of $\sigma^2 a$. The pressure Q at the top of the exclusion zone rises from 0 in these units to become the same as P, as R is increased.

the tightly curved ($R = 0$) limit. This latter limit of the grafting surface pressure is of course equal to that obtained from the exact solution: however, the two pressure profiles do not agree elsewhere in the layer. We also note that, in this limit, the pressure jump encountered at the top of the layer, $\Delta p = a\sigma R/(2V)$, is negligible compared to the pressure drop throughout the layer.

(g) Free Energy. Having described the structure of the convex layer, we turn now to calculation of the free energy. This is simplified by the observation that the change in the free energy effected by the addition of a single chain to a layer is independent of where its free end is placed.[4] This free energy, computed from (2) evaluated for the chain with free end at x_Q for ease of computation, is

$$S = \int_0^V \mathrm{d}v\,\left[\frac{a}{2}\left(\frac{\mathrm{d}x}{\mathrm{d}v}\right)^2 + p(x(v))\right] = \left(\frac{a}{2}\right)^{1/2}\int_Q^P \mathrm{d}p\,\left(-\frac{\mathrm{d}x}{\mathrm{d}p}\right)\frac{2p-Q}{(p-Q)^{1/2}} = [R+h]\left(\frac{Qa}{2}\right)^{1/2}\times [F(\pi/2,(1-Q/P)^{1/2}) - cPE(\pi/2,(1-Q/P)^{1/2})] \quad (35)$$

The second term is obtained from the first by first noting that due to the conservation of energy, $(a/2)(\mathrm{d}x/\mathrm{d}v)^2 - p = -Q$, which allows the Lagrangian to be replaced by the quantity $2p - Q$. The same result allows the integration variable to be changed from $\mathrm{d}v$ to $\mathrm{d}x$. Introduction of the known $\mathrm{d}x/\mathrm{d}p$ allows the integration variable to be transformed again to $\mathrm{d}p$. To compute the total free energy, we must build up the layer from zero coverage. The total free energy per area of the layer is thus

$$F(\sigma_0) = \int_0^{\sigma_0} \mathrm{d}\sigma\, S(\sigma) \quad (36)$$

This free energy due to the addition of a chain can be broken into pieces that are analytic and nonanalytic at $h_0/R = 0$. Defining $k = (1 - Q/P)^{1/2} = 2e^{-R/h_0} + \mathcal{O}(e^{-2R/h_0})$ and $k' = (Q/P)^{1/2}$, we note that the elliptic integrals E and F have the behaviors[27]

$$E(\pi/2,k) = \pi/2 + \mathcal{O}(k^2), \quad F(\pi/2,k) = \pi/2 + \mathcal{O}(k^2)$$

$$E(\pi/2,k') = 1 + \mathcal{O}(k^2\log[4/k]), \quad F(\pi/2,k') = \log\,[4/k] + \mathcal{O}(k^2\log[4/k])$$

for small k. This allows us to decompose (35) into

$$S = \frac{\pi^2 a h^2}{8V} - \frac{\pi^2 a h^2}{8V}\left[\frac{R}{h}\,\frac{((P/Q)^{1/2}-1)}{E(\pi/2,k')} + \left(1 - \frac{1}{E(\pi/2,k')}\right)\right] + [R+h]\left[\frac{Qa}{2}\right]^{1/2}\left[\frac{\pi}{2}c((PQ)^{1/2} - P) + (F(\pi/2,k) - \pi/2) - cP(E(\pi/2,k) - \pi/2)\right] \quad (37)$$

The first term apparently is analytic in an expansion in h_0/R and is the free energy obtained from the parabolic approximation,[4] while each of the other terms is manifestly nonanalytic in h_0/R. Note that these nonanalytic terms must constitute a positive correction to the parabolic result since the complete result is obtained from the parabolic result by imposing the constraint that the end density be nonnegative throughout the layer.

We now consider the free energy of a layer with fixed coverage and molecular weight, as a function of the radius of curvature. In this limit, we are interested in the free energy in terms of an expansion in h_0/R. However, the exclusion zone will generate exponentially small corrections to the free energy,[6] and thus the expansion of the free energy in h_0/R will lead to the analytic continuation of the concave layer free energy to h_0/R positive! We have explicitly verified that the portion of the areal free energy that is revealed by Taylor expansion in h_0/R is

$$F(\sigma) = \frac{\pi^2\sigma^3 Va}{24}\left[1 - \frac{3}{4}\frac{h_0}{R} + \frac{3}{4}\left(\frac{h_0}{R}\right)^2 + \mathcal{O}\left(\frac{h_0}{R}\right)^3\right] \quad (38)$$

as previously reported by Milner and Witten.[6] As reported in that paper, the exclusion zone thus makes no contribution to the elastic moduli of the flat surface.

For large curvatures, the free energy is

$$F(\sigma) = \frac{aR\sigma^2}{4}\log\frac{\sigma V}{R} \quad (39)$$

which is the leading behavior of (36) as $R \to 0$. In opposition to the behavior observed for small curvatures, for very tightly curved layers the result (39), and the portion of the free energy that is analytic in h_0/R at $h_0/R = 0$ (or alternately, the result obtained by ignoring the end exclusion zone)

$$F_a(\sigma) = \frac{\pi^2}{8}aR\sigma^2 \quad (40)$$

differ by a logarithmically diverging factor. The ratio $F/F_a \approx \log\,(h/R)$ as $h/R \to \infty$. Figure 5a shows the exact convex layer free energy as a function of h_0/R for fixed σ and V, along with the second-order Taylor expansion (38). Figure 5b shows the behavior of the free energy for very strong curvatures: only in this regime is the exact free energy appreciably different from the "analytic" portion obtained by ignoring the exclusion zone. Note that, for all radii of curvature, the analytic portion of the free energy is less than the total free energy, as argued above.

Finally, we consider the free energy of the Alexander–de Gennes approximation, in which all of the free ends are constrained to lie at the outer limit of the layer.[28] The

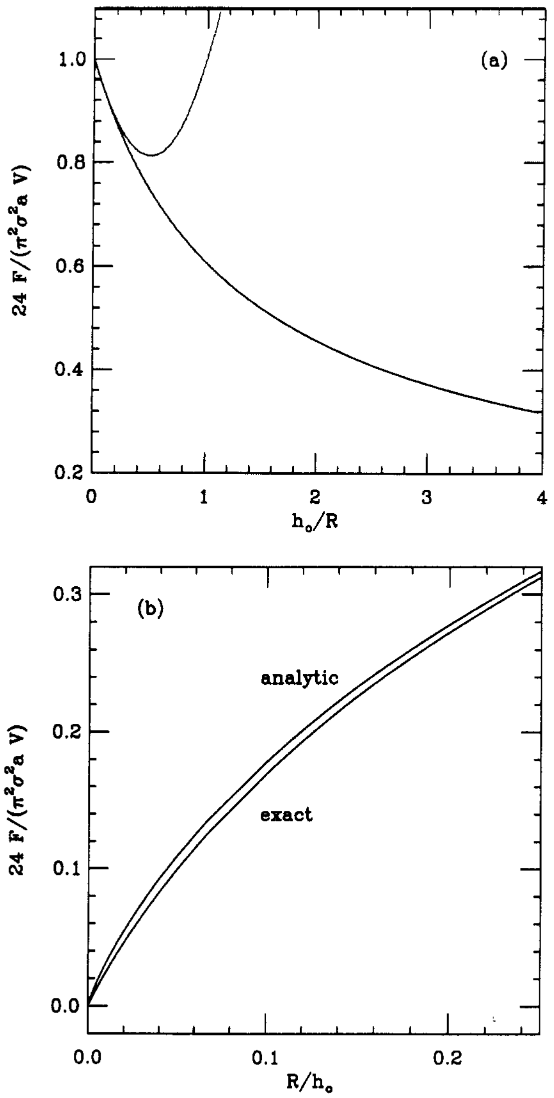

Figure 5. Free energy of the grafted layer with fixed grafting density, σ, and chain volume V as a function of curvature h_0/R. (a) Free energy for small curvature. The lower curve indicates the exact result, while the upper curve is the analytic portion to second order in h_0/R. The analytic portion to infinite order is indistinguishable from the exact result on this graph. (b) Free energy at large curvatures. The analytic free energy is the result obtained by relaxing the constraint that the end density be strictly nonnegative and thus is smaller than the (constrained) exact result. The difference between these results is appreciable only for strong curvatures ($R/h_0 < 0.02$), but the ratio of these two results diverges logarithmically in R as R is taken to zero.

action can be computed in closed form

$$S = \frac{aV}{2}\frac{\sigma^2}{(1 + h/R)^2} + a\sigma R \log\,(1 + h/R) \qquad (41)$$

and from it the free energy is obtained via (36). In the flat limit, the free energy is $F = a\sigma^3V/2$, which is a factor $12/\pi^2$ larger than the exact result.[3] In the $R = 0$ limit, the exact free energy (39) is recovered, reflecting the fact that the end-free region contains all of the stretch (i.e., all of the pressure drop). For all intermediate curvatures, this approximation has a larger free energy than does the exact result, reflecting the variational principle that the solution of the integral equation must have the lowest free energy of all normalized nonnegative end distributions.

IV. Effect of Solvent and of Spherical Curvature

In this section, we discuss the application of the ideas developed in sections II and III to cases where a grafted layer is in contact with a solvent and for the case where the surface is spherical. We stress that for these cases, as well as for the cylindrical melt, there is a region of applicability of our "classical" theory: namely, the polymers should in general be extended well beyond their free radius of gyration but should not be stretched near to their maximum extension. These limits are made quantitative in section V: for the present we assume that our description is suitable.

As remarked previously, if a grafted melt is immersed in a solvent, the monomer density will no longer be a constant but rather will be a function of the local pressure and will generally be a fraction ϕ of the melt density. Much of our development through (11) remains valid, provided we continue to interpret p as the work required per chain volume to insert a section of chain at a given height. The work per unit total volume, ϕp, is the osmotic pressure. We consider here the case of a marginal solvent where the local concentration or volume fraction ϕ is proportional to the quantity p

$$\phi = \alpha p \qquad (42)$$

where α is a constitutive constant with the dimensions of a volume. The only change in the formalism of section II is in the form of (10), which must be modified to reflect that the fraction of space filled is proportional to the pressure, namely

$$[1 + x/R]\phi = \left[\frac{a}{2}\right]^{1/2}\int_0^p \frac{\mathrm{d}p'}{(p - p')^{1/2}}\frac{\mathrm{d}\sigma}{\mathrm{d}p'} \qquad (43)$$

Upon inversion, we obtain

$$\frac{\mathrm{d}\sigma}{\mathrm{d}p} = \left[\frac{2}{\pi^2 a}\right]^{1/2}\int_0^p \frac{\mathrm{d}p_0}{(p - p_0)^{1/2}}\frac{\mathrm{d}}{\mathrm{d}p}\,(\alpha p[1 + x/R])_{p_0} \qquad (44)$$

while (8) holds without modification.

Combination of (8) and (44) yields the analogue of (13) relating the free end density to the transit time in the exclusion zone

$$\frac{\pi a R}{4\alpha p}\frac{\mathrm{d}\sigma}{\mathrm{d}p} = \left(\frac{a}{2}\right)^{1/2}\frac{R + h}{\sqrt{p}} + \frac{1}{2\pi}\int_Q^P \mathrm{d}p'\,\frac{\mathrm{d}V}{\mathrm{d}p'}(K(p,p') + S(p,p')) \qquad (45)$$

where K is the melt kernel of (14) (which has a logarithmic divergence at $p = p'$), and S is a nondivergent function of p'/p:

$$S(p,p') = \frac{1}{2}\left(1 - \frac{p'}{p}\right)K(p,p') + \left(\frac{p'}{p}\right)^{1/2} \qquad (46)$$

In Figure 6, the functions $K(p,p')$ and $S(p,p')$ are plotted as functions of $z = p'/p$. Although we have not yet solved (45), we anticipate behavior quite similar to that in the case of the melt, as the singularity of the kernel and the structure of the integral equation as a whole are markedly similar to (13). In particular, we believe that a exclusion zone of finite height survives the addition of solvent, even in the case of an arbitrarily large radius of curvature.

The most important property of the integral equation (45) is that it is linear. Additionally, we find that the kernels K and S are functions of only p'/p, which suggests a change of variable to $s = \log p$ to cast the equation into the form of a convolution. Since we know the exact solution to the cylindrical melt, we anticipate finding the correction to the solution due to the addition of the nondivergent solvent kernel using rather conventional numerical techniques for the solution of linear integral equations.

If the grafting surface is made to be a sphere, the integral equation becomes nonlinear in $\mathrm{d}V/\mathrm{d}p$ in both the melt and solvent cases. In both cases, this complication arises

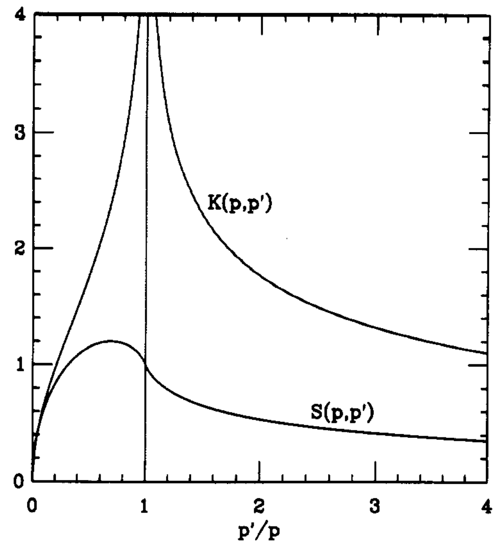

Figure 6. Melt kernel $K(p,p')$ of (14) and solvent correction $S(p,p')$ as a function of $z = p'/p$. The logarithmic singularity of K is apparent, while S is finite for all z, although the slope of S diverges logarithmically at $z = 1$. Note that the melt kernel K is larger than the solvent contribution S for all z, although both go to zero as $2\surd z$ as $z \to 0$.

because the geometrical factor $[1 + x/R]$ in the cylindrical volume equation for the melt (9) and for the solvent (43) must be replaced by $[1 + x/R]^2$ for a spherical grafting surface, where R is now the sphere radius. The linear dependence of each factor of x on $\mathrm{d}V/\mathrm{d}p$ (as evidenced by (8)) leads to an integral equation quadratic in $\mathrm{d}V/\mathrm{d}p$. The derivations of the analogues of (13) and (45) are straightforward, and only the results are stated below. In the case of the melt, the packing relation (18) is replaced by

$$3\sigma V R^2 = (R + h)^3 - R^3 \qquad (47)$$

which tells us the grafting density σ required us to fill the spherical layer of height h with chains.

For the case of the spherical melt, the integral equation is

$$\frac{\pi a}{4}\frac{R}{2}\frac{\mathrm{d}\sigma}{\mathrm{d}p} = \left(\frac{a}{8}\right)^{1/2}\frac{R}{2}\frac{[1 + h/R]^2}{\sqrt{p}} + \int_Q^P \frac{\mathrm{d}p'}{2\pi}\frac{\mathrm{d}V}{\mathrm{d}p'}K(p,p') - \frac{1}{\pi^2 R}\left(\frac{8}{a}\right)^{1/2}\int_Q^P \mathrm{d}p'\,\frac{\mathrm{d}V}{\mathrm{d}p'}\int_Q^P \mathrm{d}p''\,\frac{\mathrm{d}V}{\mathrm{d}p''}K_S(p,p',p'') \qquad (48)$$

while in the presence of solvent, it is

$$\frac{\pi a}{4\alpha p}\frac{R}{2}\frac{\mathrm{d}\sigma}{\mathrm{d}p} = \left(\frac{a}{2}\right)^{1/2}\frac{R}{2}\frac{[1 + h/R]^2}{\sqrt{p}} + \int_Q^P \frac{\mathrm{d}p'}{2\pi}\frac{\mathrm{d}V}{\mathrm{d}p'}(K(p,p') + S(p,p')) - \frac{1}{\pi^2 R}\left(\frac{8}{a}\right)^{1/2}\int_Q^P \mathrm{d}p'\,\frac{\mathrm{d}V}{\mathrm{d}p'}\int_Q^P \mathrm{d}p''\,\frac{\mathrm{d}V}{\mathrm{d}p''} \times (K_S(p,p',p'') + S_S(p,p',p'')) \qquad (49)$$

The spherical kernels for the melt (K_S) and for solvent (S_S) cases are

$$K_S(p,p',p'') = \int_0^{\min\{p,p',p''\}} \frac{\mathrm{d}p_0}{2}\left[\frac{p' - p_0}{(p - p_0)(p'' - p_0)}\right]^{1/2} \qquad (50)$$

$$S_S(p,p',p'') = \left(1 - \frac{p''}{p}\right)K_S(p,p',p'') + \left(\frac{p'p''}{p}\right)^{1/2} - \frac{2}{p}\Omega(p,p',p'')$$

where

$$\Omega(p,p',p'') = \int_0^{\min\{p,p',p''\}} \frac{\mathrm{d}p_0}{2}\left[\frac{(p - p_0)(p' - p_0)}{(p'' - p_0)}\right]^{1/2}$$

The integrals are elementary but lead to complicated expressions that mask their basic property of being nonnegative. The integral representations also allow us to conclude that K_S has a logarithmic divergence of the form $-\log |p - p''|$ for $p' \geq \max\{p,p'\}$, while S_S is nondivergent. This is reminiscent of the properties of the linear kernels K and S for the problem of the cylindrical layer.

Some comments on the form of (48) and (49) are in order. First, we note that, in both cases, ignoring terms of order R^{-1} leads precisely to the integral equations for the cylindrical melt and solvent cases ((13) and (45)) with the radius of cylindrical curvature R replaced by half of the sphere radius. This reflects the fact that $[1 + x/R]^2 = 1 + 2x/R + \mathcal{O}(x/R)^2$; i.e., the linear part of the integral equation is precisely the same in the cylindrical and spherical cases providing we take $R_c = R_s/2$. Thus, the solutions to the nonlinear equations for spheres may be considered to be effectively cylinders (to lowest nontrivial order in R^{-1}) for large R: the nonlinear terms constitute corrections that are due specifically to the spherical geometry.

If we consider the integral equations order by order in $1/R$, we find the equations for the flat layer at order R, for the cylinder (of radius $2R$) at order R^0, and for the sphere of radius R at order $1/R$. Unfortunately, one of the major points of this paper is that solving the equations order by order in R starting with the exact solutions to the flat case is not a systematic approach to the exact solutions to the cylindrical case. The logarithmic divergence of the nonlinear spherical melt kernel K_S might similarly preclude the construction of a $1/R$ expansion about the exact solution of the cylindrical case.

V. Validity of the Strong-Stretching Assumption

In the preceding sections we have described a theory for polymers grafted to curved surfaces. Central to the applicability of these ideas is the notion that the chains be strongly stretched, i.e., that the layer thickness is much larger than the free radius of gyration $R_G = (V/2a)^{1/2}$. However, the chains must not approach their maximum extension. These conditions are summarized as

$$(V/a)^{1/2} \ll h \ll Vc \qquad (51)$$

where c is a constitutive constant with units of inverse area, which converts the molecular volume to the maximum extension (c^{-1} is comparable to the cross-sectional area of one of the monomer units). For a nearly flat layer, i.e., a layer where $R \gg h$, where R is the radius of curvature, the layer thickness $h \approx V\sigma$, and thus condition (51) reduces to $(V/a)^{1/2} \ll V\sigma \ll Vc$. As long as the area per graft σ^{-1} is much larger than the cross-sectional area of the molecules c^{-1}, our approach describes the $V \to \infty$ limit precisely.

In the case that the layer is immersed in a solvent, the layer height must be determined by balancing the stretch and interaction contributions to the total free energy. We can estimate the free energy per chain as a function of the layer height:

$$F(h) = \frac{ah^2}{V} + \frac{w\phi^2\mathcal{V}}{\mathcal{N}} \qquad (52)$$

The first term is the stretch energy, while the second term is due to interactions between the chains for a layer of total volume $\mathcal{V}$, containing $\mathcal{N}$ chains each of volume V;

the volume fraction of monomer in terms of these quantities is thus $\phi = \mathcal{N}V/\mathcal{V}$. The interaction constant w has dimensions of an inverse volume and is inversely proportional to the constitutive constant, α, of section IV.

For a nearly flat layer of total area A in contact with solvent, $\mathcal{V} = Ah$ and $\mathcal{N} = A\sigma$. The free energy is $F = ah^2/V = w\sigma V^2h^{-1}$, and thus the h that minimizes it scales as $h = (w\sigma/a)^{1/3}V$. Condition (51) becomes

$$(V/a)^{1/2} \ll (w\sigma/a)^{1/3}V \ll Vc \tag{53}$$

indicating that the strong-stretching assumption is valid again for low grafting density and long chain length.

For a "comb" polymer, i.e., the tightly curved cylindrical melt ($R \ll h$), the layer thickness $h \approx (2R\sigma V)^{1/2}$, and (51) becomes

$$(V/a)^{1/2} \ll (R\sigma V)^{1/2} \ll Vc \tag{54}$$

This result indicates that as $V \rightarrow \infty$ (which implies $h/R \rightarrow \infty$), our analysis is valid provided $a^{-1} \ll R\sigma$. In physical terms, this condition is that the packing length should be much larger than the typical distance between chains along the comb. This is somewhat of an underestimate of the domain of applicability of the comb results: we know from (39) that the stretch energy of a chain diverges as log V for any curvature R and grafting density σ. This logarithmic divergence of the free energy is due to the high pressures (and strong stretching) encountered in the exclusion zone. This implies that our description of the comb geometry always is valid in the end-free zone as $V \rightarrow \infty$.

A comb of length L has a volume of $\mathcal{V} = \pi h^2L$ and contains $\mathcal{N} = 2\pi RL\sigma$ chains. Constructing the free energy for the case of immersion in solvent as above and minimizing it in order to determine h leads to the condition that

$$(V/a)^{1/2} \ll (wR\sigma/a)^{1/4}V^{3/4} \ll Vc \tag{55}$$

Evidently the comb in solvent is always in the strong-stretching regime in the limit of high molecular weight.

For the star limit ($R \ll h$) of the spherical melt, the layer thickness is

$$h = R[(3\sigma V/R + 1)^{1/3} - 1] \tag{56}$$

which behaves as $h \approx R^{2/3}(\sigma V)^{1/3}$ for $V \rightarrow \infty$. Equation 51 becomes

$$(V/a)^{1/2} \ll (\sigma V)^{1/3}R^{2/3} \ll Vc \tag{57}$$

for $h \gg R$. Clearly the limit $V \rightarrow \infty$ does not provide any stretching of the chains. The microscopic details of the star must be considered in order to decide whether the classical limit described in the previous section is appropriate.

The situation is dramatically different if the star is immersed in solvent. The star volume is $\mathcal{V} = 4\pi h^3/3$, and the number of chains in the star is $\mathcal{N} = 4\pi R^2\sigma$, which leads to the condition

$$(V/a)^{1/2} \ll (wR^2\sigma/a)^{1/5}V^{3/5} \ll Vc \tag{58}$$

We conclude that, for a star polymer in a solvent, the limit of high molecular weight guarantees that the chains are strongly stretched and that the approach of section IV is suitable.

VI. Discussion

We have described the equilibrium statistical mechanics of polymers grafted to convex surfaces, and in particular we have presented the exact solution to the mean-field theory for an incompressible melt grafted to a cylindrical surface, in the limit of strong stretching. One main result is that, as anticipated by Semenov, the structure of the convex cylindrical melt is qualitatively different from the concave cylindrical melt. In particular, the distribution of free ends is markedly different in the convex case from that in either the flat or concave cases where there are free ends throughout the layer: in the convex case, a zone from which ends are excluded appears, next to the grafting surface. The height of this exclusion zone has a dependence on R as $\exp(-R/h)$ for R much larger than the layer thickness h and thus cannot be exposed using an expansion in $1/R$.

The exclusion zone is not typically small: for $h/R = 1$, its height is about one-third of the total layer height, and in the limit of strong cylindrical curvature, the zone boundary grows to be a fraction $2/\pi$ (64%) of the layer height. The exclusion zone and its singular behavior are consequences of the physical requirement that the free end distribution be nonnegative. For the concave layer, this constraint is satisfied without requiring an exclusion zone.

A second important result is that the free energy of our exact solution (with exclusion zone) is approximated extremely well for most radii of curvature by the free energy of the solution to the equations where the end distribution is allowed to be negative. In this approximation, where the pressure varies parabolically with height, we have simple, closed-form expressions for the end and monomer distributions, the pressure throughout the layer, and the total free energy. The only limit where the exact and parabolic free energies differ strongly is in that of strong curvature, where the ratio of the two free energies behaves as log (h/R). This limit is typically not achieved anywhere in systems with varying local radii of curvature (in oil-continuous microemulsions, for example), thus this approximation may be a powerful tool in estimating the free energy of arbitrarily curved surfactant and copolymer layers. The reader should keep in mind that, though we have demonstrated the accuracy of the parabolic approximation for the cylindrical melt, we have not yet shown its accuracy in other geometries or with solvent.

We have derived the integral equation that describes the cylindrical layer immersed in a good solvent: the equation continues to be linear, and is closely related to that for the melt. Solving this problem at least numerically is a goal for the near future. We have also displayed the nonlinear integral equations for polymer layers grafted to the exterior of spheres. For both the melt and solvent cases, the nonlinearity is quadratic. To lowest nontrivial order in the inverse sphere radius $1/R$, the sphere equations reduce to the (linear) equations for cylinders of radius $R/2$. This structure may guide us to consider a $1/R$ expansion about the cylindrical solutions as a route to numerically solving the sphere equations. We anticipate that the exclusion zone will survive the addition of solvent (in the case of a cylindrical layer) and the appearance of nonlinear terms (in the case of the spherical layer). Thus, the solutions in these cases should be at least qualitatively similar to the solution for the cylindrical melt presented here. However, we again stress that the domain of applicability of the strong-stretching approximation is limited for strong spherical curvature.

Our explicit predictions are experimentally relevant to cylindrical copolymer micelles or comb polymers immersed in an excess of high molecular weight homopolymer of the same type. Our total energy calculations could be in principle used to calculate the persistence length of these cylinders and to compare this to experiment. The pressure profiles might be used to infer the potential of mean force between two such cylinders at relatively long ranges. This could be compared to the short-distance correlations observed in scattering from melts of cylinder-forming copolymer in excess homopolymer. A more direct test of this pressure profile could be made by introducing trace amounts of labeled oligomers into the system. These would be depleted near the centers of the cylinders because of the pressure there. This depletion could be detected, e.g., in scattering cross-correlations between the grafting surface and the labeled species. In a similar way chains with labeled ends could be used to detect the presence of the exclusion zone. The distribution of monomer alignments could be measured by analyzing the quadrupolar splittings of the nuclear magnetic resonance of suitably deuterated chains. Such tests would be useful in order to see how closely the predictions are obeyed at realistic molecular weights and grafting densities.

We conclude by noting that the behavior of polymers when their ends are confined to a surface has proven to be unexpectedly rich. The self-consistent stretching of the polymers produces a veritable menagerie of structures and chain configurations. In the present work we have seen how the simple feature of convex curvature leads to the spontaneous decomposition of the layer into two distinct zones. Remarkably, the very nonlocal constraints that give rise to these two zones may be formulated in a local way; i.e., as an electrostatics problem, controlled by the Laplace equation. The physical reason behind this formal locality remains unclear. What *is* clear is that end-confined polymers in more general cases, such as those of nonuniform curvature or mixtures of different types of chains, will reveal further striking behavior.

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