Density Profile of Terminally Attached Polymer Chains

Paul Venema

*Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden,
P.O. Box 9502, 2300 RA Leiden, The Netherlands*

and Theo Odijk*

*Department of Polymer Technology, Faculty of Chemical Engineering, Delft University of Technology,
P.O. Box 5045, 2600 GA Delft, The Netherlands (Received: August 28, 1991)*

Scaling theory hypothesizes a step-function profile for the segment density of polymer chains terminally attached to a planar wall. Using a self-consistent-field theory we give a perturbation analysis of the first-order correction to the step-function profile in order to gauge the impact of a possible tail. The new profile decays smoothly to zero without a discontinuity in the derivative (except near the wall). The segment density profile as scaled by the amplitude of the step-function profile has a tail that decays essentially as $1/\beta z^{*2}$, with β a dimensionless parameter and z^* the distance from the wall scaled by the step length of the step-function profile. A scaling analysis would yield $z^{*-4/3}$.

Introduction

We consider long and monodisperse, flexible polymer chains in a good solvent, which are chemically attached by one end to a (planar) wall. We assume that the density of grafts at the surface is high enough, so that the chains tend to stretch away from the surface. Our concern is to investigate the density profile $\varphi(z)$ of the segments as a function of the distance z from the wall. This problem has been addressed by several authors. Scaling arguments of Alexander[1] and de Gennes[2] hypothesize a step-

function profile for the segment density. The theory of Milner, Witten, and Cates,[3] who use the analogy of a strongly stretched chain to the trajectory of a classical particle, predicts a parabolic profile. An identical result was also found independently by Zhulina et al.[4] by a minimization of the conformational free energy

(1) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 977.

(2) De Gennes, P. G. *J. Phys. (Paris)* **1976**, *37*, 1443; *Macromolecules* **1980**, *13*, 1069.

(3) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.

(4) Zhulina, E. B.; Borisov, O. V.; Pryamitsin, V. A. *J. Colloid Interface Sci.* **1990**, *137*, 495.

of a polymer chain in the brush.

Although the scaling theory and the mean-field theories differ with respect to the predicted segment profiles, it so happens that they give identical scaling behavior for the thickness h of the brush. This scales as $h \simeq l^{2/3}\sigma^{1/3}w^{1/3}N$ with l the segment length, σ the grafting density, w the excluded-volume between the segments, and N the total number of segments in the chain. The N dependence seems well established in view of the experimental work of Auroy et al.[5] The proportionality of h with the number (N) of segments in both types of theory signifies an in the main *linear propagation* of each chain away from the wall. In the scaling picture this comes about because each macromolecule is viewed as a sequence of impenetrable blobs;[2] transverse fluctuations are weak.[2] In the mean-field theories the propagation of a chain from the wall to the brush tip is implicit either in the "classical trajectory"[3] or in the chain "stretching function".[4]

Both scaling and mean-field theories suffer from drawbacks. Although the correlations between all segments are correctly accounted for in the scaling analysis,[1,2] at least in principle, the blobs are all assumed to have the same density despite the inhomogeneity of a grafted chain. In the mean-field approaches[3,4] which are formulated at fairly low segment densities, the correlations between widely separated segments of a chain are quite adequately taken into account because the problem reduces to a chain propagating in one dimension. In that case, mean-field arguments become valid again. But local segment correlations pose a three-dimensional problem and are described rather poorly. At the chain extremities none of the theories behave as they should. Near the wall there should be a depletion layer, whereas, far from it, the segment profile ought to bear a tail decaying to zero monotonically without a discontinuity in its derivative. A resolution of all these problems is beyond the scope of this paper. Rather, our modest purpose is to investigate one of these items: the occurrence of tails.

In the first version of this paper we were led to suspect the viability of the parabolic profile[3,4] for it often did not agree with numerical work. However, we recently became aware of careful self-consistent lattice calculations by Wijmans, Zhulina, and Scheutjens[6] showing that the parabola does result but only when N becomes extremely large. Moreover, there are significant tails even for relatively large values of N. It is impossible for us to develop a complete self-consistent-field theory for the tails in view of the publishing schedule of this special issue. However, in section II we do sketch a possible WKB approach to the problem.

A second analytical line of attack is to regard the uniform scaling profile of Alexander and de Gennes as a zero-order theory. The first-order correction to it decays smoothly to zero far away from the wall and will be calculated within the context of a self-consistent-field theory in section III. We emphasize that we are not claiming to present a complete analysis of the whole profile but merely a semiquantitative perturbation theory for the tail.

WKB Approximation to the Self-Consistent-Field Theory

The self-consistent-field theory of Edwards[7] connects the segment profile $\varphi(\vec{r})$ with the Green function $G(\vec{r},\vec{r}',n)$ denoting the unnormalized probability of finding segment n at point $\vec{r}$, when one end of the test chain starts at $\vec{r}'$. For grafted chains the problem of finding G is assumed to reduce to a one-dimensional one involving the distance z from the wall. At fairly low densities $G(z,z',n)$ satisfies an equation of the diffusion type

$$\frac{\partial G}{\partial n} - \frac{l^2}{6}\frac{\partial^2 G}{\partial z^2} + w\varphi(z)G = 0 \qquad (1)$$

with $\lim(n{\to}0)\ G(z,z',n) = \delta(z-z')$ and segment density:[7]

$$\varphi(z) = \frac{\sigma \int_0^N \int_0^\infty dn\ dz'\ G_w(0,z',n)\ G(z,z',N-n)}{\int_0^\infty dz'\ G_w(0,z',N)} \qquad (2)$$

The Green function $G_w(0,z,n)$ pertains to a sequence of segments with one end fixed to the wall whereas $G(z,z',n)$ describes an unattached sequence. Because the wall is impenetrable, G is zero at the wall.

In the analytical theories[3,4] (which do not use eq 1 as a starting point), the chains "propagate" from the wall to the brush tip; i.e., each chain follows a "classical trajectory". Presumably the WKB approximation is one way of deriving this path and the nearby fluctuations. Anticipating the WKB approximation we write

$$G(z,z',n) = a(z,z'n)e^{-S(z,z',n)} \qquad (3)$$

where S is the "action" and a is a slowly varying function. We substitute this expression in eq 1, setting $l = 1$:

$$\frac{\partial a}{\partial n} - \frac{\partial a}{\partial n}\frac{\partial S}{\partial n} + w\varphi a + \frac{1}{6}\left\{2\frac{\partial a}{\partial z}\frac{\partial S}{\partial z} - a\left(\frac{\partial S}{\partial z}\right)^2 + a\frac{\partial^2 S}{\partial z^2} - \frac{\partial^2 a}{\partial z^2}\right\} = 0 \qquad (4)$$

In ref 8 the WKB treatment of the Schrodinger equation involves a similar expression. But it contains imaginary arguments so that it separates into two equations. The formal analogy between quantum mechanics and diffusion allows us to conjecture a similar separation:

$$\frac{\partial a}{\partial n} + \frac{1}{6}\left\{a\frac{\partial^2 S}{\partial z^2} + 2\frac{\partial a}{\partial z}\frac{\partial S}{\partial z}\right\} = 0 \qquad (5)$$

$$\frac{\partial S}{\partial n} + \frac{1}{6}\left(\frac{\partial S}{\partial z}\right)^2 - w\varphi = 0 \qquad (6)$$

We have deleted $\partial^2 a/\partial z^2$ as in the quantum mechanical case.[8] Equation 6 is the analogue of the classical Hamilton–Jacobi equation and is equivalent to Newton's law of motion. After multiplication of eq 5 by a it can be written in the form of a conservation law:

$$\frac{\partial a^2}{\partial n} + \frac{\partial}{\partial z}\left(\frac{1}{3}a^2\frac{\partial S}{\partial z}\right) = 0 \qquad (7)$$

Equation 6 is a nonlinear integrodifferential equation, which is coupled to eq 7 because φ still depends on a via G. Despite the considerable simplification embodied in the WKB analysis, the first two terms of eq 6 still define a diffusive rather than a propagating mode (in the quantum mechanical case the resulting Hamilton–Jacobi equation would have yielded a trajectory even when $\varphi = 0$). Hence propagation must somehow arise from the predominance of the last term involving the self-consistent potential. From the numerical work of ref 6 we expect a propagating mode with $z = f(n)$ as $N \to \infty$. At present we suspect that the integrand G_wG in eq 2 acquires a sharp maximum for a value of $z = f(n)$ as $N \to \infty$ but we have not yet solved satisfactorily eq 6 under this assumption. We hope to return to this problem in the future.

Density Profile with Continuous Derivative

In this section we concentrate on finding a smooth density profile $\varphi(z)$ by approximately solving the self-consistent-field equations by a more physically motivated method. We start from the following ansatz: the Alexander–de Gennes step-function profile is a justifiable zero-order approximation, since it gives the right scaling behavior for the brush height and in this paper we concentrate on the tails only. If we neglect the very few transverse chain fluctuations the problem is in essence a polymer chain confined within an imaginary tube perpendicular to the wall. Recall that the chain is effectively a sequence of impenetrable

(5) Auroy, P.; Auvray, L.; Leger, L. *Physica A* **1991**, *172*, 269; *Macromolecules* **1991**, *24*, 2523.

(6) Wijmans, C. M.; Zhulina, E. B.; Scheutjens, J. M. H. M. Self-Consistent-Field Theories for Polymer Brushes. Lattice Calculations and Asymptotic Analytical Description. *Macromolecules*, in press.

(7) Edwards, S. F. *Proc. Phys. Soc.* **1965**, *85*, 613. Dolan, A. K.; Edwards, S. F. *Proc. R. Soc. London A* **1975**, *343*, 427.

(8) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics*; Pergamon Press: 1977; p 51.

blobs. Accordingly, the chain may be said to propagate from the wall to the tip because the blobs cannot interpenetrate. The surface of the tube is formed by the neighboring polymers. The test chain is stretched because it cannot cross the tube surface. We model the tube as a cylinder and use cylindrical coordinates $\vec{r} = (z,\rho)$ (ignoring the angular coordinate) with the z-coordinate perpendicular and the ρ-coordinate parallel to the wall. The surface of the cylindrical tube is defined by $\rho = $ constant. End effects are disregarded altogether in the Alexander–de Gennes profile which depends on ρ and is a step function in the z-direction.

Writing the self-consistent field equation in cylindrical coordinates, we have

$$\frac{\partial G}{\partial n} - \frac{1}{6}\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho\frac{\partial G}{\partial \rho}\right) - \frac{1}{6}\frac{\partial^2 G}{\partial z^2} + w\varphi(\rho,z)G = 0 \qquad (8)$$

where $G = G(z,z',\rho,\rho',n)$ and φ is a functional of G and G_w given by

$$\varphi(\rho,z) = \frac{\int_0^N \int dn \, d\vec{r}'' \, G_w(\vec{r}',\vec{r},n) \, G(\vec{r},\vec{r}'',N-n)}{\int d\vec{r}'' \, G_w(\vec{r}',\vec{r}'',N)} \qquad (\vec{r}' \in \text{wall}) \quad (9)$$

We temporarily ignore the boundary condition $\lim(n \to 0) \, G(\vec{r},\vec{r}',n) = \delta(\vec{r}-\vec{r}')$, which is possible since we are dealing with long polymer chains. Since we are not interested in the depletion layer, we forget about the requirement $G = 0$ at the wall. The zero-order solution to the self-consistent-field equations yielding a uniform brush equivalent to the scaling theory of Alexander and de Gennes is denoted by $G_0(\rho,\rho',n)$. Within the brush G_0 satisfies the following equation

$$\frac{\partial G_0}{\partial n} - \frac{1}{6}\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho\frac{\partial G_0}{\partial \rho}\right) + w\varphi_0(\rho)G_0 = 0 \qquad \text{for } 0 \leq z \leq h$$
$$(10)$$

where h is the brush height and the zero-order density profile φ_0 is independent of z. Outside the brush G_0 and φ_0 are simply given by

$$G_0 = 0 \quad \text{and} \quad \varphi_0 = 0 \qquad \text{for } z > h \qquad (11)$$

Since we are interested in the coarse-grained profile $\varphi(z)$ it is unnecessary to evaluate $G_0(\rho,\rho',n)$ explicitly so that the zero-order problem is basically a black box. The main point is that in the following analysis it turns out that we need merely the height h of the brush and its amplitude $\bar{\varphi}$ which are both predicted by the scaling theory of Alexander and de Gennes. Accordingly, our treatment must be viewed as a zero-order scaling picture perturbed by z-dependent effects calculated by a self-consistent-field method even though G_0 itself is couched in SCF language.

We now average the expressions 8 and 10 across a section of the tube:

$$\frac{\partial\langle G\rangle}{\partial n} - \frac{1}{6}\frac{\partial^2\langle G\rangle}{\partial z^2} + w\langle\varphi(\rho,z)G\rangle = 0 \qquad (12)$$

$$\frac{\partial\langle G_0\rangle}{\partial n} + w\langle\varphi_0(\rho)G_0\rangle = 0 \qquad \text{for } 0 \leq z \leq h \qquad (13)$$

with

$$\langle ... \rangle = \frac{\int\int ...\rho\rho' \, d\rho' \, d\rho}{\int\int \rho\rho' \, d\rho' \, d\rho} \qquad (14)$$

where we have used $G_0(\rho,\rho',n) = g_0(\rho)g_0(\rho')e^{\mu n}$ and $G(\rho,\rho',z,z',n) = g(\rho) \, g(\rho') \, H(z,z')$, where the decomposition in the z- and ρ-directions is suggested because the Green function varies on a much smaller scale in the ρ-direction ($\simeq \sigma^{-1/2}$) than in the z-direction (scale $\simeq \sigma^{1/3}w^{1/3}N$). Furthermore, we have assumed that $\partial g(\rho)/\partial \rho = 0$ and $\partial g_0(\rho)/\partial \rho = 0$ on the tube boundary so that the second terms vanish in eqs 8 and 10.

In order to calculate the first-order correction to the step-function profile we postulate the following form for the averaged Green function $\langle G\rangle$.

$$\langle G(z,z',\rho,\rho',n)\rangle = \langle G_0(\rho,\rho'n)\rangle H(z,z') \qquad \text{for } 0 \leq z \leq h \quad (15)$$

$$\langle G(z,z',\rho,\rho')\rangle = c_0 H(z,z') \qquad \text{for } z > h \qquad (16)$$

with c_0 a constant independent of n. Substituting eqs 15 and 16 in eqs 12 and using eqs 11 and 13 we get

$$-\frac{1}{6}\frac{\partial^2}{\partial z^2}H + w(\varphi(z) - \bar{\varphi})H = 0 \quad \text{for } 0 \leq z \leq h \qquad (17)$$

$$-\frac{1}{6}\frac{\partial^2}{\partial z^2}H + w\varphi(z)H = 0 \qquad \text{for } z > h \qquad (18)$$

where we have defined

$$\varphi(z) \equiv \frac{\langle\varphi(\rho,z) \, g(\rho)\rangle}{\langle g(\rho)\rangle} \quad \text{and} \quad \bar{\varphi} \equiv \frac{\langle\varphi_0(\rho) \, g_0(\rho)\rangle}{\langle g_0(\rho)\rangle} \qquad (19)$$

Both $\bar{\varphi}$ and h in the above equations are given by the scaling theory of Alexander and de Gennes:

$$h \simeq w^{1/3}\sigma^{1/3}N \qquad (20)$$

$$\bar{\varphi} \simeq w^{-1/3}\sigma^{2/3} \qquad (21)$$

If we are dealing with long enough chains it is reasonable to suppose that the function $H(z,z')$ may be factorized as

$$H(z,z') \simeq \Psi(z)\cdot\Psi(z') \qquad (22)$$

Note that this is not the ground-state solution but a zero-order estimate close to it and valid if end effects are small and presumably justifiable in our perturbation analysis because G turns out to be close to G_0. Interesting this in eq 9 we find for the segment density φ:

$$\varphi(z) \simeq N\Psi^2(z) \qquad (23)$$

The constant c_0 has been chosen to make φ continuous and $g_0^2(\rho)$ and $g^2(\rho)$ are densities normalized to unity. Combining eqs 18, 19, 22, and 23 leads to the following nonlinear differential equation for Ψ:

$$\frac{1}{6}\frac{\partial^2}{\partial z^2}\Psi = w(N\Psi^2 - \bar{\varphi})\Psi \qquad \text{for } 0 \leq z \leq h \qquad (24)$$

$$\frac{1}{6}\frac{\partial^2}{\partial z^2}\Psi = wN\Psi^3 \qquad \text{for } z > h \qquad (25)$$

It is convenient to rewrite these in terms of scaled variables as

$$\frac{\partial^2}{\partial z^{*2}}\Psi^* = \beta(\Psi^{*2} - 1)\Psi^* \quad \text{for } 0 \leq z^* \leq 1 \qquad (26)$$

$$\frac{\partial^2}{\partial z^{*2}}\Psi^* = \beta\Psi^{*3} \qquad \text{for } z^* > 1 \qquad (27)$$

with the scaled variables and β defined as

$$\Psi^* = \left(\frac{N}{\bar{\varphi}}\right)^{1/2}\Psi; \quad z^* = z/h;$$

$$\varphi^* = \varphi/\bar{\varphi}; \quad \beta \simeq h^4/N^2 \simeq N^2\sigma^{4/3}w^{4/3} \qquad (28)$$

Note that in the expression for β a factor 6, originating from eqs 24 and 25, has been incorporated in the $\simeq$ sign. We now have to solve eqs 26 and 27 as a function of the parameter β with the boundary conditions that Ψ^* and its derivative be continuous at $z^* = 1$ and Ψ^* vanishes as $z^* \to \infty$. We furthermore demand that

$$\int_0^\infty \varphi(z) \, dz = N\sigma \qquad (29)$$

The general solution to eq 26 is given by[9]

$$\Psi^*(z^*) = C \, \text{cn} \, (\lambda(z^* - z_0^*),k) \qquad (30)$$
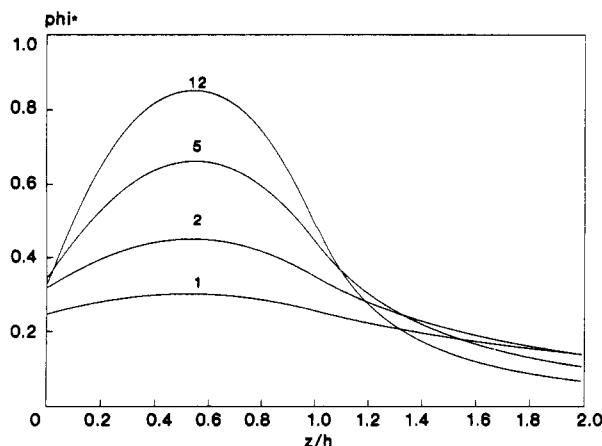
Figure 1. Scaled segment density $\varphi^* = \varphi/\bar{\varphi}$ as a function of the scaled distance from the wall $z^* = z/h$ for $\beta = 1$, 2, 5, and 12.
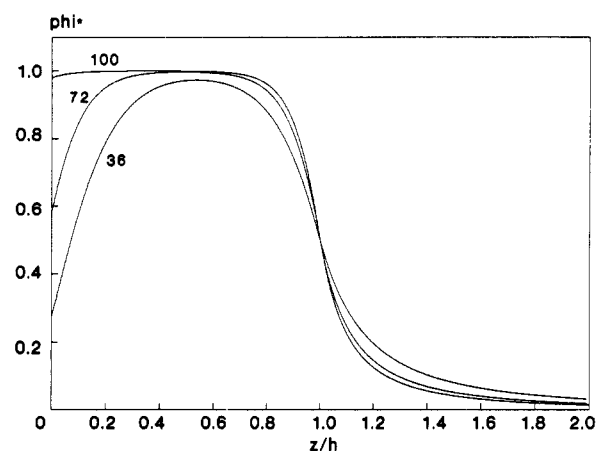

Figure 2. Scaled segment density $\varphi^* = \varphi/\bar{\varphi}$ as a function of the scaled distance from the wall $z^* = z/h$ for $\beta = 36$, 72, and 100.

Figure 3. Scaled segment density $\varphi^* = \varphi/\bar{\varphi}$ as a function of the scaled distance from the wall $z^* = z/h$ for $\beta = 50$ and 90.

Figure 4. Comparison between the scaled segment density profiles for $\beta = 5$ and 12 and the parabolic profile proposed by Milner, Witten, and Cates.

Here cn denotes one of the elliptic functions of Jacobi. The integration constants C, λ, and k have to satisfy the relation

$$k^2 = \frac{\lambda^2 - \beta}{2\lambda^2} \quad \text{and} \quad C^2 = \frac{\beta - \lambda^2}{\beta} \qquad (31)$$

Since C and k are functions of λ, it is clear that there are two independent integration constants. The solution to eq 27, with the boundary condition $\Psi \to 0$ as $z \to \infty$, is simply given by

$$\Psi^*(z^*) = \left(\frac{2}{\beta}\right)^{1/2} \frac{1}{z^* + B} \qquad (32)$$

with B an integration constant. The integration constants are to be determined from the boundary conditions as a function of the parameter β. We hae done this numerically and some typical results are shown in Figures 1–3, where we have plotted the resulting scaled segment density φ^* ($=\Psi^{*2}$) as a function of the scaled distance z^* for representative values of β.

Discussion

In the limit of $\beta \to \infty$, i.e., $N \to \infty$, the step-function profile is obtained, which is to be expected because we perturb from this profile. For β larger than about 50 (cf. Figures 2 and 3) a plateau is still discernible in the segment profile. If we suppose our entire profile to be taken literally, then this agrees with the molecular dynamics calculations of Murat and Grest.[10] Further reduction of β (cf. Figure 1) leads to a smoother decay, while at $\beta \approx 12$ the decay in a certain region of z^* is close to a parabolic profile proposed by Milner, Witten, and Cates.[3] Nevertheless, the likeness
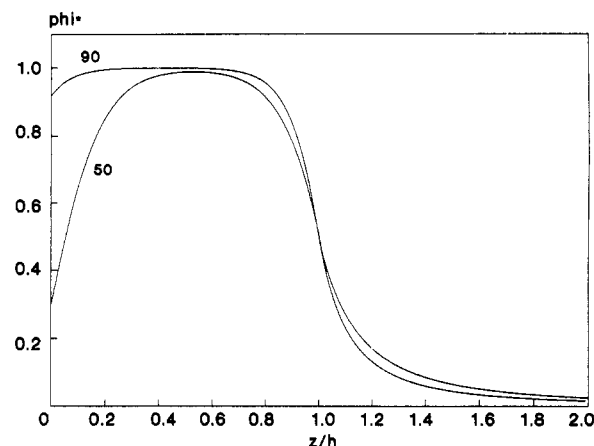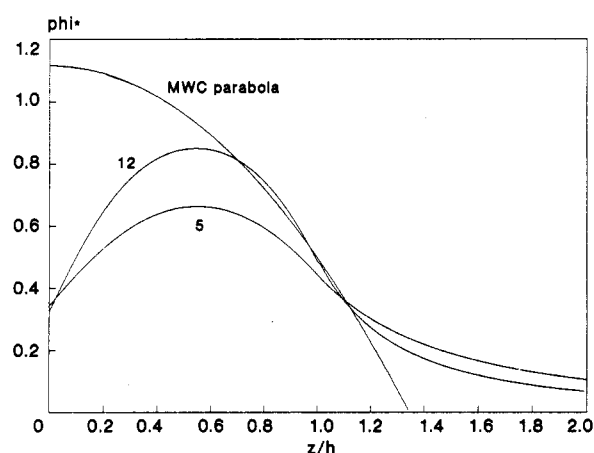
deteriorates rapidly when β starts to deviate from this value. For comparison we have plotted our predictions for two different values of β together with the parabolic approximation in Figure 4. We note that the deviations from the parabolic profile beyond the maxima in our curves are similar to those found in the numerical simulations.[3,11] Values of β below about 5 (Figure 1) will only occur for a physically unrealistic choice of the parameters σ, w, and N. However, these detailed comparisons may be of limited value; our emphasis is on the occurrence of tails and the zero-order Alexander–de Gennes profile may be a poor starting point in, say, the middle of the brush.

Defining the start of a tail as the point of inflection ($z^* = 1$ in our calculation) we observe that generally a tail has an amplitude of about one-third of the maximum of the profile. The length of the tail decreases as β increases, but the influence of the tail on the total profile is still much larger than one might expect. Using the same definition, we find a similar behavior of the tails in numerical work.[6,10–12] To compare our results with the numerical calculations we had to calculate the parameter β from estimates of the parameters N, σ, and w; β typically varies between 10 and 100.

In summary we conclude that the density profile of grafted chains must have substantial tails. The tails in the scaled segment density profile φ^* decay essentially as $1/\beta z^{*2}$ with β, a dimensionless parameter. This parameter equals the square of the ratio of the square brush height to the mean square extension length. The tails are especially significant for β smaller than 100, a range of values often met in practice. The profile approaches zero smoothly, i.e., without a discontinuity in the derivative which must

(9) Davis, H. T. *Introduction to Nonlinear Differential and Integral Equations*; Dover Publications: New York, 1962; p 207.
(10) Murat, M.; Grest, G. S. *Macromolecules* **1989**, *22*, 4054.

(11) Chakrabarti, A.; Toral, R. *Macromolecules* **1990**, *23*, 2016.
(12) Whitmore, M. D.; Noolandi, J., *Macromolecules* **1990**, *23*, 3321.

be so since the derivatives of the Green function are continuous except near the wall. Near the brush tip the chains become more diffuse so that the profile tends to be similar to that valid for the usual adsorbed polymer, at least within the limitations of our perturbation analysis.

Since our starting eqs 8 and 9 are of the mean-field type, the decay of the tails ($\approx 1/\beta z^{*2}$) is also a mean field result. In order to heuristically improve upon this one may follow a method proposed by de Gennes.[13] We know that the mean-field correlation length $\xi_m \cong (wN\Psi^2)^{-1/2}$ must be replaced by $\xi_s \cong (wN\Psi^2)^{-3/4}$ valid in scaling theory ($l = 1$). Hence, an expression like eq 27 becomes

$$\frac{\partial^2}{\partial z^{*2}}\Psi^* = \beta_s \Psi^{*4} \qquad \text{for } z^* > 1 \qquad (33)$$

(13) De Gennes, P. G. Macromolecules 1981, 14, 1637.

with $\beta_s \cong h^5/N^3$. As a consequence we find tails decaying as $z^{*-4/3}$. The exponent of this decay is the same as that of the profile of a nongrafted polymer solution in contact with a adsorbing wall as given by de Gennes[13] assuming a self-similar structure.

When the tails are appreciable we expect our perturbation treatment to be fairly reliable beyond the inflection of the profile. We regard the occurrence of a large depletion zone at small β to be an artifact since we use the "bare" Green function for the first-order correction which does not account for the presence of the wall. Again we stress that the Alexander–de Gennes ansatz is at best approximate and certainly not the only viable zero-order theory useful in evaluating tails.

Diffusion Past an Entropy Barrier

Robert Zwanzig

Laboratory of Chemical Physics, Building 2, National Institute for Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20892 (Received: September 3, 1991)

Diffusion in a tube or channel of varying cross section has been treated, by Fick and Jacobs, as one-dimensional diffusion past an entropy barrier determined by the tube cross-sectional area or channel width. The Fick–Jacobs diffusion equation is rederived, along with corrections involving the curvature of the tube or channel. On comparison with two exactly solvable examples, the Fick–Jacobs equation appears to be quite reliable as long as the curvature is not too great.

Introduction

This paper deals with a method, described by Jacobs,[1] for treating diffusion in a tube of varying cross section. For an illustration see Figure 1, which shows a cylindrical tube with a bulge in the middle. Suppose for example that a solute molecule starts out at one end of the tube. How long does it take to arrive at the other end? If there is no change in the tube diameter, the problem is essentially one dimensional in character and is easily solved. But if there is a bulge, the molecule's random walk through the tube is slowed in the vicinity of the bulge because of the extra space that it finds available for exploration. A constriction in the tube has the same effect; extra time is required to find the way through the bottleneck. Any change in shape appears to retard diffusion.

Jacobs gave an essentially one dimensional treatment of such two or three dimensional problems. We give here a new derivation of Jacobs' approach and investigate its limits of validity.

Questions of this sort come up in various contexts. One example is concerned with the rate of passage of ions through a channel in a phospholipid membrane.[2] Another example was discussed recently[3] in connection with a model of a chemical reaction in which the kinetics was dominated by passage through a bottleneck rather than passage over a potential barrier. A third example is Brownian motion of a polymer subject to rigid constraints; this example is due to Fixman.[4] (The present paper is a development of his ideas in a different context.)

The Fick–Jacobs Equation

Jacobs,[1] in his book *Diffusion Processes*, gave a heuristic derivation of an effective one-dimensional diffusion equation, referred to here as the Fick–Jacobs (or F–J) equation. (Jacobs attributed his treatment to Fick.[5]) As far as I am aware, this material is not presented in any of the other standard references on diffusion theory.

In Jacobs' treatment, the center line of the tube is the x axis, and the cross-sectional area of the tube at x is $\mathcal{A}(x)$. (In two dimensions, the tube is replaced by a channel, and $\mathcal{A}(x)$ is replaced by its width.) The total amount of solute in a cross sectional slice of thickness dx, at x, at time t, is $G(x,t)$ dx; this is the integral of the local concentration $C(x,y,z,t)$ over the cross-sectional slice of volume $\mathcal{A}(x)$ dx. At equilibrium, $C(x,y,z,\text{eq})$ is a constant concentration, and so $G(x,\text{eq})$ is proportional to $\mathcal{A}(x)$. The F–J equation is

$$\frac{\partial}{\partial t} G(x,t) = D \frac{\partial}{\partial x} \mathcal{A}(x) \frac{\partial}{\partial x} \frac{G(x,t)}{\mathcal{A}(x)} =$$
$$D \frac{\partial^2}{\partial x^2} G(x,t) - D\frac{\partial}{\partial x} \frac{\mathcal{A}'(x)}{\mathcal{A}(x)}G(x,t) \quad (1)$$

Note that the correction to simple diffusion due to changes in shape is first order in $\mathcal{A}'(x)$.

The F–J equation has exactly the same structure as the Smoluchowski equation for diffusion in a one-dimensional potential $U(x)$ if we use the correspondence (omitting irrelevant constants)

$$\mathcal{A}(x) \leftrightarrow e^{-U(x)/kT} \qquad (2)$$

But since $\mathcal{A}(x)$ does not contain any temperature, being only an area or width, it appears more reasonable to connect $\mathcal{A}(x)$ to an entropy $S(x)$ rather than a potential $U(x)$, according to

$$\mathcal{A}(x) \leftrightarrow e^{S(x)/k} \qquad (3)$$

Then we can say that the F–J equation describes diffusion past an entropy barrier.

The word "barrier" is used in the sense of an obstacle to passage from one place to another. It does not imply that the entropy is

(1) Jacobs, M. H. *Diffusion Processes*; Springer: New York, 1967; p 68.
(2) Gates, P.; Cooper, K.; Rae, J.; Eisenberg, R. *Prog. Biophys. Mol. Biol.* 1990, 53, 153.
(3) Zhou, H.-X.; Zwanzig, R. *J. Chem. Phys.* 1991, 94, 6147.
(4) Fixman, M. *J. Chem. Phys.* 1978, 69, 1527.
(5) Fick, A. *Poggendorfs Ann.* 1855, 94, 59.