On the Self-Similar Structure of Adsorbed Polymer Layers: Dependence of the Density Profile on Molecular Weight and Solution Concentration

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ABSTRACT: We show that the self-consistent-field theory to describe polymer adsorption on solid–liquid interfaces (Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619) behaves, for long chains and high adsorption affinities, qualitatively as predicted by scaling theory (de Gennes, P.-G. *Macromolecules* **1981**, *14*, 1637): a proximal regime of a single lattice layer is followed by a remarkable self-similar region in the semidilute (central) part of the profile which crosses over to an exponential decay in the distal regime. For finite bulk volume fraction ϕ^b we find the expected mean-field dependence $\phi(z) \sim z^{-2}$ for infinite chain length r, but in general the power law is more complex and depends on both ϕ^b and r: $\phi(z) \sim z^{\alpha}$, where $\alpha = -2 + \text{const}(\ln \phi^b)/r^{0.5}$. The distal regime is exponential: $\phi(z) = \beta \exp(\gamma z)$, where γ has a similar dependence on $\ln \phi^b$ and r and β is a function of α and γ. From our mean-field analysis we propose that the de Gennes scaling picture of the adsorbed polymer layer is only correct for infinitely long chains. When ϕ^b is low and the chain length not extremely large, the exponent in the self-similar profile deviates strongly from the mean-field value −2 and, analogously, is expected to deviate from the scaling prediction $-^4/_3$.

Introduction

Over the last 2 decades many theories to describe the equilibrium behavior of homopolymers adsorbed from solutions onto a solid interface have been developed. Among them two schools have emerged and lived more or less side by side. The first school, pioneered by de Gennes,[1,2] applies the so-called scaling approach. It is characterized by a maximum of physics in as few computations as possible. The second one uses the self-consistent-field (SCF) theory proposed by Scheutjens and co-workers.[3,4] This computationally more laborious approach provides a large number of detailed predictions, which sometimes prevents one from grasping the main physics. The aim of this paper is to show that under most conditions the SCF density profiles in the polymer layer next to a surface are characterized by three regimes, like in scaling. These three regimes were first defined by de Gennes: a proximal regime dominated by polymer–surface contacts, a central regime with a self-similar behavior, and an exponential profile in the distal regime. The two approaches give different predictions for the relevant scaling powers in good solvents. In short, de Gennes predicts a power law regime independent of the bulk volume fraction ϕ^b and of chain length r: $\phi(z) \sim z^{-4/3}$, whereas, as we will prove, the SCF approach predicts in the limit of infinitely long chains a profile of the form $\phi(z) \sim z^{-2}$ in the semidilute part of the profile. Up to now no scaling analysis of the SCF results has been published, but as we will show below some very interesting conclusions can be deduced from it. We hope that our observations will be useful for understanding the scaling behavior of polymer layers in general.

Theory

Scaling Theory. de Gennes recognizes three regimes in the equilibrium adsorbed layer profile:

1. Proximal Regime. The density profile near the wall is dominated by segment–surface contacts, making the behavior of the polymers near the wall very system specific.

2. Central Regime. The arguments leading to the correct scaling start from the correlation length in semidilute polymer solutions $\xi(\phi) \sim \phi^{-3/4}$. Next, a generalized correlation length $\xi(z) \sim (\phi(z))^{-3/4}$ in the adsorption profile is defined which should be proportional to z (so $\xi(z) \sim z$) because there is no other length scale in the polymer layer. Combining these observations leads directly to the well-known universal self-similar structure: $\phi(z) \sim (\xi(z))^{-4/3}$ or

$$\phi(z) \sim z^{-4/3} \tag{1}$$

In other words, the local correlation length in the profile is simply the distance to the wall; the "blobs" or mesh sizes near the wall grow linearly with z outward.

3. Distal Regime. The outer part of the profile for $\phi(z)$ smaller than the overlap concentration $\phi^* \sim r^{-4/5}$ falls off exponentially:

$$(\phi(z) - \phi^b) \sim \phi^b \exp(-z/\xi^b) \tag{2}$$

where the superscript b refers to the bulk solution.

Self-Consistent-Field Theory. The SCF density profile follows from the (mean-field) lattice partition function for the system. We will briefly review the main approximations included in the formalism. In lattice sites equally sized chain segments and solvent molecules are positioned. The lattice is composed of flat layers numbered $z = 1, ..., M$. On one side ($z = 0$) an impenetrable wall limits the configurational space of the molecules, whereas on the other side of the system, at layer $z = M$, a reflecting boundary minimizes any effects of the finite size of the system. The parameter M should be large enough to ensure that the bulk values are reached. A local mean-field approximation in the lattice layer allows an easy evaluation of the local potentials

$$u_i(z)/kT = u'(z) + \chi_{ij}(\langle\phi_j(z)\rangle - \phi_j^{\,b}) - \delta(1,z)\,\chi_s \tag{3}$$

for both types of molecules i and j in the system (solvent or polymer). In eq 3 three contributions can be distinguished. The first term, $u'(z)$, is a Lagrange parameter which ensure that each lattice layer is completely filled.

The second term, which contains the familiar Flory–Huggins interaction parameter χ, accounts for the polymer–solvent interaction, and the third term, containing the Silberberg χ_s parameter, reflects the energetic effect of displacing a polymer segment by a solvent molecule on the surface (thus, by definition, $\chi_s = 0$ for the solvent).

Next, the Boltzmann factor $G_i(z) = \exp(-u_i(z)/kT)$ (also called the free segment distribution function) is defined for both the polymer segments and the solvent molecules. The recurrence relations

$$G_i(z,s|1) = \langle G_i(z,s-1|1)\rangle\, G_i(z) \tag{4a}$$

$$G_i(z,s|r) = \langle G_i(z,s+1|r)\rangle\, G_i(z) \tag{4b}$$

ensure chain connectivity for segment s in layer z. In this way, both the chain end distribution functions $G_i(z,s|1)$ (starting from the first segment) and $G_i(z,s|r)$ (starting from the other end) are related to the free segment distribution functions $G_i(z) = G_i(z,1|1) = G_i(z,r|r)$. The angular brackets in eqs 2 and 3 indicate an average over three layers $z - 1$, z, and $z + 1$ according to a (lattice-type-dependent) a priori step probability to go from z to $z - 1$, to do a step within a layer, and to step from z to $z + 1$, respectively. Equation 3 implies a first-order Markov approximation. The combination of the two chain end distribution functions gives the segment density profiles:

$$\phi_i(z,s) = (\phi_i^{\mathrm{b}}/r_i)G_i(z,s|1)\, G_i(z,s|r)/G_i(z) \tag{5}$$

The division by the free segment distribution function $G_i(z)$ is needed to correct for double counting of segment s, and ϕ_i^{b}/r_i is the proper normalization. A stationary point, also called the self-consistent profile, is found by solving numerically the coupled implicit eqs 3–5 with the boundary condition that in each layer the total volume fraction $\sum_i \phi_i(z) = 1$. The summation over all segments of the chain molecule leads to the overall polymer segment density profile: $\phi_i(z) = \sum_s \phi_i(z,s)$.

Methods

The results presented in this paper are computed by the standard SCF approach first published in 1979 by Scheutjens and Fleer.[3] The computer program optimized for long chain molecules was written by Scheutjens.[5] Unless stated otherwise we used a cubic lattice, a Flory–Huggins χ parameter set equal to zero (good solvent), and a Silberberg χ_s parameter equal to 1. This value is above the critical value χ_{sc} which represents the transition from depletion to adsorption. The self-consistency of the segment density profile with the segment potential profile was achieved numerically. In all cases the precision of the results is at least seven significant digits.

Results

In this section we will present a scaling analysis of the SCF profiles. These are mainly calculated with $\chi_s = 1$, where we find clear scaling behavior. However, as the situation changes considerably on lowering the adsorption affinity, a small paragraph is devoted to values of χ_s nearer to the critical value.

High χ_s. Figure 1 is a typical illustration of the various regimes found in the SCF adsorption profile. The self-similar regime shows up as a straight line in the log–log representation (in this case extending from layer number 2 up to about layer number 50), whereas the exponential part of the profile gives a linear behavior on a log–lin plot (layers 30–350). The transition between the self-similar and exponential regimes takes place somewhere between layers 30 and 50 at z'. Detailed calculation, as given below, yields $z' = 39$. This value is indicated in Figure 1 by an arrow. The volume fraction in the first layer deviates from the straight line in the log–log plot (Figure 1a). Thus, the proximal regime can in this case be identified as being the very first layer adjacent to the interface.

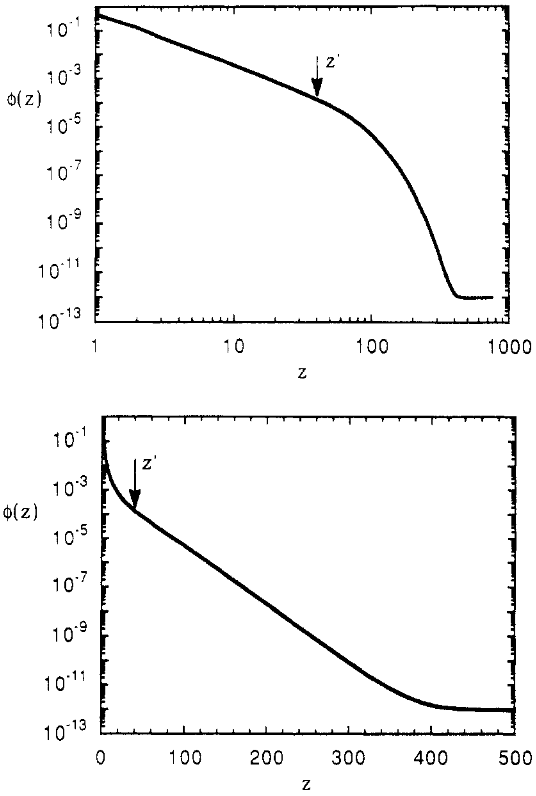

Figure 1. Volume fraction profile for a system with $r = 50\,000$ and $\phi^{\mathrm{b}} = 10^{-12}$, $\chi = 0$, $\chi_s = 1$, cubic lattice: (a) log–log plot, (b) log–lin plot. The transition point z' between the central and distal regimes is indicated by an arrow.

Contrary to the prediction of de Gennes' theory, however, the scaling powers found in plots like Figure 1a,b are dependent on bulk volume fraction ϕ^{b} and chain length r.

It has been well recognized that the SCF scheme given by Scheutjens et al., is equivalent to the "diffusion equation" approach pioneered by Edwards[6] and used in detail by, for instance, Jones and Richmond[7] and Ploehn et al.[8] in the context of polymer adsorption. In the SCF approach Cohen Stuart already predicted that the following power law behavior is expected for the semi-dilute part of the density profile:[9]

$$\phi(z) \sim z^{-2} \tag{6}$$

The power -2 can be related to the correlation length first given by Edwards for mean-field chains in the semidilute regime:[10] $\xi(\phi) \sim \phi^{-1/2}$. Demanding $\xi(z)$ to scale with z as in scaling theory yields the equation above. Equation 6 should indeed be the natural limit for infinite chain length in a mean-field theory. We show in the appendix that the Ploehn approach, which uses the same field equation, also provides this power law for long chains. We now take a more general form for the central regime:

$$\phi(z) \sim z^{\alpha} \qquad (1 < z \le z') \tag{7}$$

where the "crossover" distance z' will be defined more precisely below. The exponent α is taken to be of the general form

$$\alpha = -2 + f(r,\phi^{\mathrm{b}}) \tag{8}$$

where f should vanish for infinite chain length.

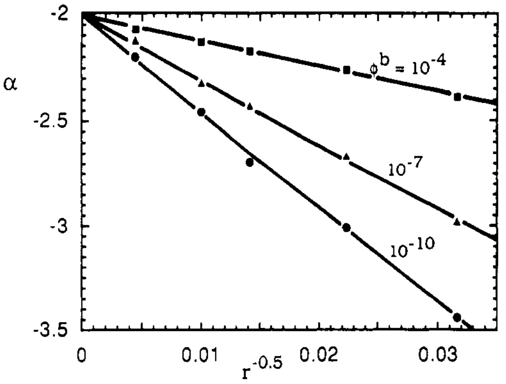

Figure 2. Power law exponent α in the central regime as a function of $r^{-0.5}$. The values of the bulk volume fraction ϕ^b are (squares) 10^{-4}, (triangles) 10^{-7}, and (circles) 10^{-10}. $\chi = 0$, $\chi_s = 1$.

In the distal regime, the profile falls off exponentially:

$$\phi(z) \sim \beta e^{\gamma z} \qquad (z' \leq z \leq XR_g) \qquad (9)$$

where X is of order unity and R_g is the radius of gyration of the chain.

In order for the exponent to be dimensionless, we need $\gamma \sim (\xi^b)^{-1}$, where $\xi^b \sim R_g$ is the length scale in the dilute regime. In a mean-field theory $R_g \sim r^{0.5}$ (ideal chains). We rewrite eq 2 so that $\ln \phi^b$ enters the exponent:

$$\gamma \sim \ln \phi^b / r^{0.5} \qquad (10)$$

When $\phi(z) = \phi^b$, the distal regime ends and crosses over to the bulk. This discontinuity occurs at very low volume fractions and is not a serious problem.

The requirement that at z' the profile should be continuous leads to

$$z' = \alpha/\gamma \qquad (11)$$

and to

$$\beta \sim (\alpha/\gamma)^\alpha e^{-\alpha} \qquad (12)$$

For extremely low bulk volume fractions we expect the power law regime to vanish and thus z' to be of order unity for all r. This suggests f and γ to have a similar chain length and bulk volume fraction dependence:

$$f \sim \ln \phi^b / r^{0.5} \qquad (13)$$

Note that both f and γ are 0 for infinite chain length at finite ϕ^b.

Using the lattice calculations by varying chain lengths and bulk volume fractions, we found from plots like Figure 1 the exponents α and γ in the central and distal regime, respectively, as a function of the chain length. Results are plotted in Figures 2 and 3, where the abscissa scale is $r^{-0.5}$ as suggested by eqs 10 and 13. It can be seen that indeed these exponents are linear in $r^{-0.5}$. The scatter in Figure 2 is due to the small number of layers that form the central regime, especially for short chains. At given r, α and γ are found to increase proportionally with $\ln \phi^b$, which is also in agreement with eqs 10 and 13. Hence, we can now specify the numerical coefficients in the parameters α and γ:

$$\alpha = -2 + 1.87(\ln \phi^b)/r^{0.5} \qquad (14)$$

and

$$\gamma = (-4.45 + 0.3 \ln \phi^b)/r^{0.5} \qquad (15)$$

Equations 14 and 15 are found for a cubic lattice. Changing the lattice will only alter the numerical coefficients. Together with eqs 7, 9, and 12 and replacing all the proportionality signs with equality signs, they present analytical expressions for the SCF profiles for $\chi_s = 1$ and $\chi = 0$.

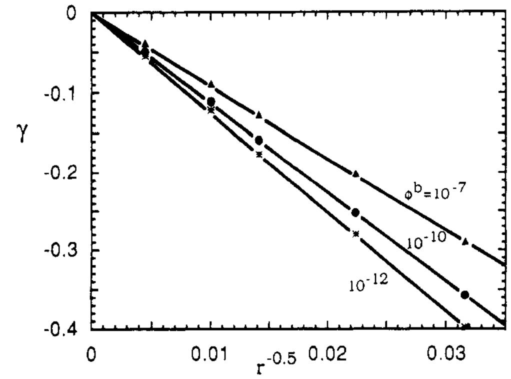

Figure 3. Slope γ as found in plots like Figure 1b in the distal regime as a function of $r^{-0.5}$. Bulk volume fractions: (triangles) 10^{-7}, (circles) 10^{-10}, (stars) 10^{-12}. $\chi = 0$, $\chi_s = 1$.

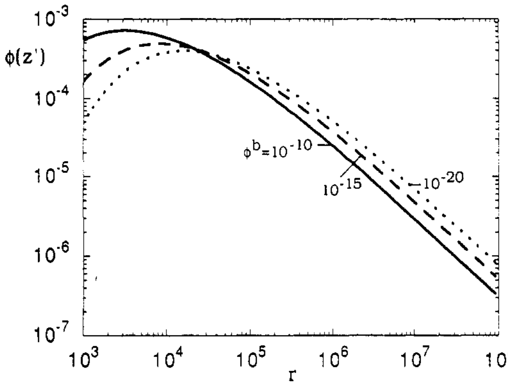

Figure 4. Crossover volume fraction as a function of chain length, as calculated using eqs 6, 10, 13, and 14: (full line) $\phi^b = 10^{-10}$, (dashed line) $\phi^b = 10^{-15}$, (dotted line) $\phi^b = 10^{-20}$.

Combining eqs 7, 11, 14, and 15, we can calculate $\phi(z')$, the volume fraction at which crossover from semidilute to dilute behavior takes place, as a function of chain length r. Using the analytical expressions it is possible to predict $\phi(z')$ for higher chain lengths than by using the original numerical procedure. The result is shown in Figure 4. We see that the curves exhibit a maximum at a certain chain length referred to as r', which is higher for lower solution concentrations. For $r < r'$ the power law regime is too narrow to be physically relevant. Working out the numerical values, we find that $r' \approx 0.4(\ln \phi^b)^2$. Scaling behavior, of the type $\phi(z') \sim r^{-x}$ is only found for r well above r'. Scaling theory[1] states that the crossover from the semidilute to dilute regime will take place at the overlap concentration $\phi^* \sim r^{-4/5}$. For mean-field chains the crossover concentration $\phi^* \sim r^{-1}$. de Gennes identified the transition from the central to the distal regime in the adsorption profile as the overlap concentration.[2] As can be seen from Figure 4, we find the proper mean-field scaling $\phi(z') \sim r^{-1}$ only for very high chain length ($r > 10^7$). Note that there is also a dependence of $\phi(z')$ on $\ln \phi^b$.

χ_s near χ_{sc}. The scaling theory for polymer adsorption by de Gennes is restricted to the so-called weak coupling limit. In our lattice approach this would imply that $\chi_s < 1$. All results given above are for $\chi_s = 1$. In Figure 5 we collect some density profiles for long chains ($r = 50\,000$) and $\phi^b = 10^{-12}$ with varying adsorption affinities. We first discuss the difference found between $\chi_s = 1$ (full curve) and $\chi_s = 0.4$ (dashed curve). In contrast to $\chi_s = 1$, the central regime for $\chi_s = 0.4$ does not show a clear power law behavior. The proximal regime is larger than one layer, and the profile is less steep. This behavior has been

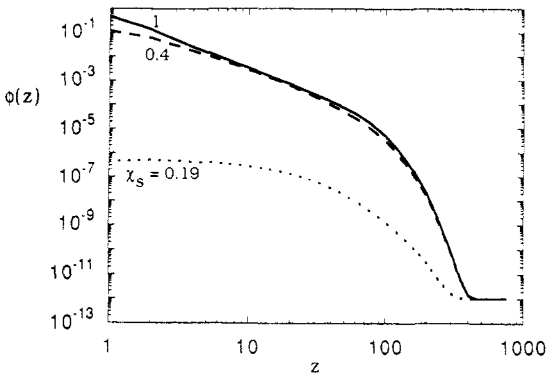

Figure 5. Volume fraction profiles for systems with $r = 50\,000$ and $\phi^b = 10^{-12}$, $\chi = 0$, cubic lattice: (full line) $\chi_s = 1$, (dashed line) $\chi_s = 0.4$, (dotted line) $\chi_s = 0.19$.

predicted by de Gennes and Pincus in an analysis of the proximal exponent.[11] The crossover to the central regime is smooth. In this case, for a full analysis computations for much larger chain lengths are needed to unravel the possible chain length and ϕ^b dependence of the proximal part of the profile.

The dotted curve in Figure 5 is for $\chi_s = 0.19$, close to the critical value of 0.182 for a cubic lattice. In this case the de Gennes and Pincus picture is not valid any longer. We even find a maximum in the segment density profile at layer $z = 2$. A similar maximum was found by Roe[12] in 1966 for an isolated polymer chain near a weakly adsorbing wall. There is no power law region nor an exponential regime. It should be noted that near χ_{sc} and for low ϕ^b, the surface densities are too low to justify a local mean-field approximation.

For $\chi_s > 1$, the profile is almost equal to the profile with $\chi_s = 1$ (not shown). The only differences are in the occupancies in the first two layers, which increase with increasing adsorption energy (although always $\phi(1) < 1$). The slopes in the central and distal regimes are not affected at all.

We summarize that scaling behavior is only found for high values of the adsorption energy parameter χ_s. This is in contrast to de Gennes' conjecture that it should be valid for weak adsorption.

Discussion

From the results summarized in eqs 13 and 14 we can check that the density profiles fall off to the bulk values always at shorter distances than about $3R_g$ and for most practical cases shorter than $2R_g$, i.e., the chain diameter. This seems a more natural limit than the de Gennes picture, where at $z \sim R_g$ only the crossover from the semidilute to the dilute regime is reached, and the extension of the adsorbed layer strongly depends on the value of ϕ^b and is not restricted. In the SCF model, decreasing ϕ^b has two opposite effects on the profile: the distal regime becomes wider because it takes longer to reach ϕ^b, but both $|\alpha|$ and $|\gamma|$ are larger which strongly reduces the layer thickness. Only for infinite chain length do the corrections vanish. In that case the distal regime is effectively not present and the de Gennes scaling $\phi(z) \sim z^{-4/3}$ is expected to be exact.

The $-^4/_3$ power arises from the correlation length in the semidilute regime which has been shown to be correct.[13] The SCF approach shows, for good solvents, the wrong limiting behavior because it neglects correlations. Preliminary results suggest that using the approach as given by Leermakers and Scheutjens[14] (where a rotational isomeric scheme is used in combination with anisotropic corrections for the vacancy probability as proposed by Di Marzio[15]) improves the theory in this point, but only over a short distance.

The SCF theory predicts a clear chain length and bulk concentration dependence on the segment density profile. For high χ_s and r, eqs 13 and 14 define the profiles for good solvents. It is tempting to suggest that the exact result $\phi(z) \sim z^{-4/3}$ should be generalized for finite chain length and concentration effects, in a way similar to that given in eqs 13 and 14.

Integrating the volume fraction profile in the power law regime (i.e., from $z = 1$ to z') yields a good estimate of the excess amount of polymer adsorbed Γ. For long chains $\Gamma \sim 1 + \ln \phi^b/r^{0.5}$, so that, for infinite r, Γ reaches a limiting value. This limit is similar to the de Gennes result.

Conclusions

We have found analytical expressions for the volume fraction profiles of homopolymers adsorbing on a solid interface from a good solvent and for relatively high χ_s values. The results indicate that the scaling picture of de Gennes is qualitatively correct. However, our suggestion is that the "universal" density profile $\phi(z) = z^{-4/3}$ should be corrected for effects of a finite chain length and a finite bulk solution concentration.

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Appendix

Ploehn et al.[8] developed a continuous self-consistent-field model using a ground-state approximation. Their expression for the volume fraction profile is

$$\phi(z) = \frac{4\lambda_0 c_i \exp(-(24\lambda_0)^{1/2}z)}{\left(c_i - \frac{\upsilon}{2}\exp(-(24\lambda_0)^{1/2}z)\right)^2 - \frac{2}{3}\lambda_0 w \exp(-2(24\lambda_0)^{1/2}z)} \quad \text{(A1)}$$

where

$$c_i = \frac{1}{\phi(0)}\left\{2\lambda_0^{1/2}\left[\lambda_0 + \frac{\upsilon}{2}\phi(0) + \frac{w}{6}\phi^2(0)\right]^{0.5} + \frac{\upsilon}{2}\phi(0) + 2\lambda_0\right\} \quad \text{(A2)}$$

and υ and w are excluded-volume parameters. For long chains, λ_0 is a small number, as $\exp(\lambda_0 r)$ is of order 1. Neglecting terms in λ_0, eq A2 reduces to

$$c_i = \upsilon/2 \quad \text{(A3)}$$

Substituting eq A3 into eq A1 and again neglecting terms of order λ_0 yields

$$\phi(z) = \frac{4\lambda_0}{\upsilon(-1 + \cosh((24\lambda_0)^{1/2}z))} \quad \text{(A4)}$$

By expanding the cosh term, the unity term in the denominator cancels, as well as λ_0, so that indeed for long chains $\phi(z) \sim z^{-2}$.

Analogously, for a Θ-solvent $\upsilon = 0$, so that

$$c_i^2 = \frac{2}{3}w\lambda_0 \quad \text{(A5)}$$

This leads to a sinh term in the denominator:

$$\phi(z) = \frac{(24\lambda_0/w)^{1/2}}{\sinh\,((24\lambda_0)^{1/2}z)} \qquad \text{(A6)}$$

Expanding the sinh, keeping only the lowest order in z, we find $\phi(z) \sim z^{-1}$.

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