

# Adsorption of Polymer Solutions onto a Flat Surface

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Received May 24, 1995; Revised Manuscript Received November 27, 1995<sup>®</sup>

**ABSTRACT:** We present a theoretical description of polymer adsorption from solution which is based on a mean field approximation but which goes beyond the standard ground state dominance approximation. The properties of the adsorbed polymer chains are described by two coupled order parameters. This allows a description of the chains in terms of tails and loops. When the bulk solution is dilute, the adsorbed polymer layer has a double layer structure with an inner layer dominated by loops and an outer layer dominated by tails. Explicit asymptotic forms are found for the monomer concentration profile and for the crossover distance between the loops and tail regions. The precise concentration profile is obtained by a numerical solution of two coupled differential equations. One of the surprising results is that the total polymer adsorbed amount has a nonmonotonic variation with molecular weight and decreases for large values of the molecular weight. The concentration profiles are also determined when the bulk solution is semidilute or concentrated. At any bulk concentration, the monomer concentration has a nonmonotonic variation with the distance to the adsorbing wall and shows a minimum at a finite distance. This depletion effect can be significant in the vicinity of the crossover between dilute and semidilute solutions. All the results are in agreement with the existing numerical solutions of the complete mean field theory of polymer adsorption. Excluded volume correlations are taken into account by constructing scaling laws for polymers in a good solvent both in dilute and in semidilute solutions.

## I. Introduction

Adsorbed polymer layers have attracted considerable attention in the recent years from both the experimental<sup>1</sup> and the theoretical<sup>2</sup> sides. The interest in these systems is driven by the practical applications of adsorbed polymer layers for colloidal stabilization as well as for other purposes. Adsorbed polymers are also interesting from a more general fundamental point of view as providing an example of confined polymer systems, a wider class including also grafted polymers,<sup>3</sup> periodic microstructures in polymer and block-copolymer blends,<sup>4</sup> etc.

The equilibrium structure of homopolymers reversibly adsorbed from dilute solutions was predicted theoretically many years ago in the classical papers of de Gennes<sup>5</sup> and Jones and Richmond.<sup>6</sup> Much progress has also been made recently in the description of both static and dynamic properties<sup>7</sup> of more complicated adsorbed polymer systems, including block copolymers,<sup>8</sup> polyelectrolytes,<sup>9</sup> random heteropolymers,<sup>10</sup> and irreversibly adsorbed polymers.<sup>11</sup>

Recently, we have shown using scaling arguments that the structure of adsorbed polymer layers far enough from the adsorbing surface is determined primarily by the tail of the polymer chains (end parts) rather than by the loops (the central parts of the polymer chains).<sup>12</sup> This implies that the structure of an adsorbed layer is more complex than supposed by the classical theories. The aim of the present paper is to reconsider in detail the simplest situation of reversible adsorption of neutral linear homopolymers. We mostly restrict ourselves here to a mean field approach<sup>13</sup> using a Flory–Huggins form for the interaction free energy between monomers. This approach is strictly valid for moderately dilute solutions of macromolecules in marginal solvents, a situation which is not unusual in experiments. For completeness we consider the whole concentration range from very

dilute bulk solutions to moderately concentrated solutions. In the last section, assuming that our results remain qualitatively valid, we build scaling laws that take into account the excluded volume correlations in a good solvent.

Equilibrium adsorption has been also extensively studied within the mean field approximation using a combination of theoretical and computer approaches.<sup>1</sup> An additional motivation of our work is a quantitative comparison of our predictions with the “computer” results.

The paper is organized as follows. In the next section, we outline the classical mean field theory for adsorption, which is based on the so-called ground state dominance approximation. We show that ground state dominance fails to account for the structure of the layer away from the wall; the critical (crossover) distance  $z^*$  between the regions dominated by tails and loops is much smaller than the gyration radius  $R$  of a polymer chain. We also briefly give scaling predictions for the distributions of loops and tails. A new approach valid at all distances is presented in section 3. The concentration profiles for the adsorbed layers in equilibrium with dilute and semidilute solutions obtained with the new formalism are analyzed in sections 4 and 5. The concentrated regime is considered in section 6 using a combination of different approaches. In section 7, the results are extended to polymer solutions in a good solvent.

## II. Classical Mean Field Theory of Polymer Adsorption

**A. Ground State Dominance Approximation.** We consider a solution of long polymer chains at thermal equilibrium attracted by an adsorbing wall. We assume that the bulk solution falls in the so-called marginal regime,<sup>14</sup> where the interaction free energy between monomers,  $F_{\text{int}}$ , is dominated by the second virial term:

$$F_{\text{int}} = \frac{1}{2} \nu T \int [c(\mathbf{r})]^2 d^3\mathbf{r} \quad (1)$$

where  $\nu$  is the second virial coefficient or excluded

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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, February 15, 1996.

volume between two monomers and  $c$  is the local concentration. The marginal regime requires that on the one hand the effective polymer volume fraction  $\phi \equiv cv$  is small, and on the other hand that the statistics of the polymer chains (and their fragments) is Gaussian. This last requirement is fulfilled if<sup>14,15</sup>

$$\phi \gg \left(\frac{v}{a^3}\right)^2 \quad (2)$$

where  $a$  is the monomer size and where it is assumed that  $v/a^3 \ll 1$ .

The total free energy of the solution (for a given concentration profile  $c(\mathbf{r})$ ) is the sum of the interaction contribution  $F_{\text{int}}$ , of the conformational free energy  $F_{\text{conf}}$ , and of the attractive interaction with the wall,

$$F_s = \int c(\mathbf{r}) U_s(z) d^3\mathbf{r} \quad (3)$$

The potential  $U_s(z)$  accounts here for the short range attraction of the monomers to the wall,  $z$  being the coordinate normal to the wall. The conformational term in the square-gradient approximation<sup>13,15</sup> reads

$$F_{\text{conf}} = \frac{a^2}{4} T \int \frac{(\nabla c)^2}{c} d^3\mathbf{r} \quad (4)$$

Equation 4 is valid when the characteristic wavelength associated with the spatial variations of  $c(\mathbf{r})$  is larger than  $a$ , but smaller than the gyration radius of a polymer coil,  $R = aN^{1/2}$ , where  $N$  is the number of monomers per chain (note thus that  $a$  is the chain statistical segment divided by  $\sqrt{6}$ ).

The total (grand canonical) thermodynamic potential of the system is

$$\tilde{F} = F - \mu_0 \int c(\mathbf{r}) d^3\mathbf{r}$$

The free energy is  $F = F_{\text{int}} + F_{\text{conf}} + F_s$ , and the bulk chemical potential is related to the bulk concentration  $c_0$  by  $\mu_0 = Tvc_0$ . The minimization of  $\tilde{F}$  over  $c(z)$  [in the following we assume that the system is uniform in the  $x, y$  plane] leads to the following Edwards equation<sup>17</sup>

$$-\psi'' + U_{\text{tot}}\psi = E\psi \quad (5)$$

where  $\psi'' \equiv d^2\psi/dz^2$ , and  $U_{\text{tot}}(z) = U_s(z) + U_{\text{int}}(z)$  is the total effective field acting on each monomer,  $U_{\text{int}}(z) = \delta F_{\text{int}}/\delta c(z)$  being the average molecular field. [Here and below we choose  $T$  as the energy unit and  $a$  as the unit length.] The order parameter  $\psi = \psi(z)$  is proportional to the chain end concentration. It is related to the total concentration by

$$\phi(z) = \phi_0 \psi^2(z) \quad (6)$$

The boundary conditions are  $\psi(0) = 0$  and  $\psi(\infty) = 1$ . This last condition imposes that  $E = U_{\text{tot}}(\infty) = \mu_0$ . We assume from now on that the wall attraction is short range: the potential  $U_s(z)$  is not negligible only in a thin layer close to the wall. It is well-known<sup>18</sup> that the effect of a *local* potential  $U_s(z)$  can be reduced to an effective boundary condition at  $z = 0$  (if one is interested only in the region outside the attractive layer):

$$\psi'(0)/\psi(0) = -1/b \quad (7)$$

where  $b$  is the so-called extrapolation length (inversely proportional to the adsorption strength) which depends

only on the wall potential. If we use the effective boundary condition (7), the surface contribution  $U_s$  must be omitted from the potential.

We can then rewrite eq 5 as  $-\psi'' + U\psi = 0$  where  $U = U_{\text{int}} - \mu_0 = \phi - \phi_0$ . The order parameter is then given by<sup>19</sup>

$$\psi = \coth\left(\frac{z}{2\xi} + \beta\right) \quad (8)$$

where

$$\beta = (1/2) \operatorname{arcsinh}(b/\xi); \quad \xi = a/\sqrt{2\phi_0} \quad (9)$$

$\xi$  is the bulk correlation length. The concentration profile then reads

$$\phi(z) = \phi_0 \coth^2\left(\frac{z}{2\xi} + \beta\right) \quad (10)$$

In the formal limit  $\phi_0 \rightarrow 0$  corresponding to an equilibrium with an extremely dilute bulk solution we get

$$\phi(z) = \frac{2}{(z+b)^2} \quad (11)$$

In this regime, the polymer chains are trapped near the wall and the adsorbance (surface coverage)  $\Gamma \equiv \int \phi(z) dz$  is dominated by short distances ( $z \sim b$ ) and is finite,  $\Gamma = 2/b$ .

The range of validity of the concentration profile (11), which is *formally* exact in the limit  $\phi_0 \rightarrow 0$  has not yet been discussed. The results described above are based on the so-called ground state dominance approximation,<sup>13</sup> which is not expected to be valid at distances larger than the coil size  $R$ . On the other hand, the ground state dominance approximation is valid at shorter scales,  $z \ll R$ . It is important to note, and this is one of the main messages of this paper, that there is another restriction: the profile (11) also implies that the concentration of the central parts of the chains (loops) dominates over the contribution of the end parts (tails). This restriction is analyzed below using the scaling approach used earlier in ref 12.

**B. Loops and Tails: Scaling Picture.** We first consider the distribution of chain ends,  $\rho(z) \equiv vc_e(z)$ , where  $c_e$  is the concentration of chain ends, assuming that the total concentration is given by eq 11 for  $z \lesssim R$ . In the ground state dominance formalism  $\rho(z) \propto \psi(z) \propto \sqrt{\phi(z)}$ , so that  $\rho(z) = \text{const}/(z+b)$ . The prefactor is found from the normalization condition

$$\int_0^R \rho(z) dz \simeq \frac{2}{N} \Gamma \quad (12)$$

which simply means that there are two ends per chain. The result is

$$\rho(z) \simeq \frac{4}{Nb} \left(\ln \frac{R}{b}\right)^{-1} \frac{1}{z+b} \quad (13)$$

We now take into account the fact that each *chain end* at a position  $z$  is the end point of a *tail* comprising  $g \sim z^2$  monomers. The concentration of monomers belonging to tails is thus of order  $\phi_t(z) \sim z^2 \rho(z)$ . Omitting the logarithmic factor in eq 13, we thus get in the region  $b \ll z \ll R$

$$\phi_t(z) \sim \frac{z}{Nb} \quad (14)$$

Comparing  $\phi_t$  with the loop concentration given by eq 11, we conclude that the loops are dominant at short distances from the wall  $z < z^*$ , where<sup>12</sup>

$$z^* \sim (Nb)^{1/3} \quad (15)$$

At larger distances,  $z > z^*$ , it is the tails that dominate, the contribution of loops to the total concentration being negligible. The scaling behavior of the total concentration  $\phi \simeq \phi_t$  in the region  $z > z^*$  must obey the same scaling law,  $\phi \sim 1/z^2$  as at shorter distances. This statement is extensively discussed below. However, it can be justified by the following argument. The molecular field is  $U = \phi$  in the regime under consideration. One can easily check that if the potential  $U \sim 1/z^\alpha$  were decreasing faster than  $1/z^2$  ( $\alpha > 2$ ), then the tails would leak out from the wall (the tail concentration would diverge at  $z \rightarrow \infty$ ). On the other hand a  $U$  profile with  $\alpha < 2$  would lead to a localization of tails and loops near the wall: the concentration would decay exponentially at large  $z$ . Obviously, both behaviors are inconsistent with the condition  $U = \phi$ . Therefore,  $\alpha = 2$ . Therefore  $\rho(z) \sim \phi_t/z^2 \sim 1/z^4$  in the region  $z > z^*$ , so that the loop concentration is  $\phi_l(z) \propto \rho^2(z) \propto 1/z^8$ . Assuming a smooth crossover in the region  $z \sim z^*$  we thus obtain

$$\phi_l \sim \frac{1}{z^8}; \quad \phi_t \sim \frac{z}{Nb} \quad b < z < z^* \quad (16a)$$

$$\phi_l \sim \frac{(Nb)^3}{z^8}; \quad \phi_t \sim \frac{1}{z^2} \quad z^* < z \ll R \quad (16b)$$

Thus we obtain (within the mean field approximation) an additional long-distance regime  $z > z^*$  (originally predicted in ref 12) where the tails play a dominant role. In this section, the treatment is limited to scaling laws, it is not quantitative and also does not look completely rigorous. A more quantitative formalism taking into account both loops and tails is described below.

### III. Mean Field Theory of Tails and Loops

**A. Adsorbed versus Free Chains.** We now go back to the most general mean field formulation of the adsorption problem and consider a system of ideal chains near an attractive wall, characterized by the extrapolation length  $b$  ( $b \ll R$ ) and submitted to a given external potential  $U(z)$  ( $U \rightarrow 0$  for  $z \rightarrow \infty$ ). The partition function  $Z(n, z)$  of a chain consisting of  $n$  monomers with one end point fixed at position  $z$  and the other end point free obeys the following equation<sup>15,17</sup>

$$\frac{\partial Z}{\partial n} = Z' - UZ \quad (17)$$

with the boundary condition  $(Z/Z)_{z=0} = -1/b$  and with the initial condition  $Z(0, z) = 1$ . The general solution of eq 17 is

$$Z(n, z) = \sum_s K_s \psi_s(z) \exp(-E_s n) \quad (18)$$

where  $\psi_s(z)$  and  $E_s$  are respectively the eigenfunctions and the eigenvalues of the "Schrödinger equation" associated with eq 17:  $-\psi_s'' + U\psi_s = E_s\psi_s$ . If the eigenfunctions are normalized,  $\int_0^\infty \psi_s^2(z) dz = 1$ , the closure relation fixed the amplitude  $K_s = \int_0^\infty \psi_s(z) dz$ .

In the general case, the spectrum  $E_s$  consists of a continuous branch ( $E = q^2$ ) and a set of discrete levels

( $E_s < 0$ ). In the case of adsorption, the discrete part is due to the local attraction to the wall. In the absence of molecular field ( $U = 0$ ), the discrete part would consist of only one level  $E_0 = -1/b^2$ . The molecular field, which is due to the repulsion between monomers, cannot create additional bound states but can only increase  $E_0$  (i.e. decrease  $|E_0|$ ). Therefore, in the adsorption problem, the discrete spectrum always contains only one bound state,  $E_0 = -\epsilon$ . Note that  $\epsilon$  is in fact the effective adsorption energy per monomer. Our basic assumption which is crucial for the whole formalism is that the binding energy *per chain* is large enough

$$\epsilon N \gg 1 \quad (19)$$

We will show below that this condition is satisfied if the bulk concentration is low enough.

The partition function  $Z(N, z)$  can then be represented as

$$Z(N, z) = K_0 \psi_0(z) \exp(\epsilon N) + \sum_q K(q) \psi(q, z) \exp(-q^2 N) \quad (20)$$

where the two terms in the right hand side correspond to the discrete level and to the continuous spectrum.

We now distinguish between *adsorbed* (bound) chains which have at least one monomer in contact with the adsorbing wall and *free* chains which do not have any contacts with the wall. An adsorbed chain comprises a *train*, the section including all the monomers between contacts and two *tails* including the monomers between a free end and the last or the first contact.

The partition function of a chain of  $N$  monomers can be decomposed as a sum of two terms corresponding to adsorbed and free states:

$$Z(N, z) = Z_a(N, z) + Z_f(N, z) \quad (21)$$

where the indices  $a$  and  $f$  stand for "adsorbed" and "free". Obviously, in the very vicinity of the wall,  $Z(N, 0) = Z_a(N, 0)$  since  $z = 0$  implies that the chain is in an adsorbed state; the partition function  $Z(N, 0)$ , when the condition (19) is satisfied, is dominated by the first eigenvalue in eq 20:

$$Z(N, 0) = \text{const} \exp(\epsilon N)$$

An adsorbed chain can then be divided into a tail (the first  $n$  links between the end and the first contact point with the wall) with a partition function  $Z_{\text{tail}}(n, z)$  and the rest of the chain (train + another tail) with a partition function  $Z(N-n, 0)$ . Accordingly, we write the partition function of the whole chain (with the end point fixed at position  $z$ ) as

$$Z_a(N, z) = \int_0^N Z_{\text{tail}}(n, z) Z(N-n, 0) dn = \exp(\epsilon N) Z_{\text{tail}}(z) \quad (22)$$

where

$$Z_{\text{tail}}(z) = \text{const} \int_0^N Z_{\text{tail}}(n, z) \exp(-\epsilon n) dn$$

Note that this last equation and the condition (19) impose that the cutoff number of monomers in a tail is  $n_c = 1/\epsilon \ll N$ . Therefore the upper limit in the integral can be extended to infinity, so that the function  $Z_{\text{tail}}(z)$  virtually does not depend on  $N$ .

Hence

$$Z_{\text{tail}}(z) = Z_a(N, z) \exp(-\epsilon N) =$$

$$\left\{ \lim_{N \rightarrow \infty} Z(N, z) \exp(-\epsilon N) \right\} \left\{ \lim_{N \rightarrow \infty} \frac{Z_a(N, z)}{Z(N, z)} \right\}$$

Obviously, the second limit is 1, and the first limit (see eq 20) is just  $K_0\psi_0(z)$ .

Equation 22 can then be rewritten as

$$Z_a(N, z) = \exp(\epsilon N) K_0 \psi_0(z) \quad (23)$$

The adsorbed chain contribution  $Z_a$  corresponds thus to the first term in eq 20 (bound state), and the free chain contribution  $Z_f$  to the second term (continuous spectrum).

The concentration of chain ends,  $\rho$  [note that here and below we use the volume concentration (=volume fraction) defined as the number concentration times the excluded volume,  $v$ ], is proportional to the chain partition function,  $\rho(z) = \text{const } Z(N, z)$ , where  $\text{const} = \rho(\infty) = 2\phi_0/N$  since  $Z(N, \infty) = 1$ . In particular, the concentration of end points of adsorbed chains is

$$\rho_a(z) = \frac{2\phi_0}{N} K_0 \exp(\epsilon N) \psi_0(z) \quad (24)$$

The total number of end points of adsorbed chains,  $\int \rho_a(z) dz$ , is equal to  $2\Gamma/N$ , where the adsorbance  $\Gamma$  is the total number of monomers belonging to adsorbed chains, hence

$$\phi_0 K_0^2 \exp(\epsilon N) = \Gamma \quad (25)$$

Note that this result can also be obtained by balancing the chemical potentials of the free chains in the bulk to the chemical potential of the adsorbed chains.

**B. Loops and Tails Concentration.** The total monomer concentration at point  $z$  can be calculated as

$$\phi(z) = \frac{\phi_0}{N} \int dn Z(n, z) Z(N-n, z) \quad (26)$$

Using eq 26, we write the total concentration as a sum of three terms:  $\phi(z) = \phi_l(z) + \phi_t(z) + \phi_f(z)$ , where

$$\phi_l(z) = \frac{\phi_0}{N} \int dn Z_a(n, z) Z_a(N-n, z) \quad (27a)$$

$$\phi_t(z) = \frac{2\phi_0}{N} \int dn Z_f(n, z) Z_a(N-n, z) \quad (27b)$$

$$\phi_f(z) = \frac{\phi_0}{N} \int dn Z_f(n, z) Z_f(N-n, z) \quad (27c)$$

The concentration of monomers belonging to loops, tails, and free chains are respectively  $\phi_l$ ,  $\phi_t$ , and  $\phi_f$ . Using eqs 23 and 25, we can rewrite eq 27a as  $\phi_l(z) \approx \Gamma \psi_0^2(z)$ . This last equation implies that the total number of monomers belonging to loops,  $\int \phi_l(z) dz$ , is close to  $\Gamma$ . This is consistent since the adsorbance is dominated by *short* loops and the contribution of tails is small. The difference between  $\phi_l(z)$  and  $\Gamma \psi_0^2(z)$  is due to the fact that eq 23 is valid only if  $n$  is large enough ( $n\epsilon \gg 1$ ). For smaller  $n$  eq 23 overestimates the function  $Z_a$ ; this effect can be taken into account by a renormalization of the prefactor  $\Gamma \rightarrow \Gamma_1$ :  $\phi_l(z) = \Gamma_1 \psi_0^2(z)$ , where  $\Gamma_1 = \Gamma - \Gamma_t \approx \Gamma$  is the total number of monomers per unit area belonging to loops, and  $\Gamma_t$  is the contribution of the tails.

The statement that end effects for  $\phi_l$  can be accounted for just by a renormalization of the prefactor is not trivial. However, we do not discuss this point here in more detail as this renormalization is not important for most of the results considered in the present paper. The statement is proved in the second paper of this series. Defining  $\psi(z) \equiv \sqrt{\Gamma_1} \psi_0(z)$  we obtain

$$\phi_l(z) = \psi^2(z) \quad (28)$$

The function  $\psi$  satisfies then the following equations:

$$-\psi'' + U\psi = -\epsilon\psi; \quad \psi'(0)/\psi(0) = -1/b; \quad \psi(\infty) = 0 \quad (29)$$

Using eqs 24 and 25, eq 27b, the tail concentration, can be rewritten as  $\phi_t(z) = \rho_a(z)\varphi(z)$ ,

$$\phi_t(z) = \rho_a(z)\varphi(z) = B\psi(z)\varphi(z) \quad (30)$$

where

$$B = \frac{2\Gamma}{NK}; \quad K \equiv \int \psi(z) dz \approx K_0 \sqrt{\Gamma} \quad (31)$$

$$\varphi(z) = \int dn Z_f(n, z) \exp(-\epsilon n) \quad (32)$$

According to its definition the free chain partition function  $Z_f$  satisfies the same "Schrödinger" equation as the total partition function  $Z$ :

$$\frac{\partial Z_f}{\partial n} = Z_f' - UZ_f \quad (33)$$

but with the boundary condition

$$Z_f(n, 0) = 0 \quad (34)$$

Using eqs 32–34 and taking into account the initial condition  $Z_f(0, z) = 1$ , we get

$$-\varphi'' + (U + \epsilon)\varphi = 1; \quad \varphi(0) = 0 \quad (35)$$

Equations 35 completely specify the function  $\varphi(z)$ , provided that we also take into account the boundary condition that  $\varphi$  does not diverge exponentially at  $z \rightarrow \infty$ .

**C. Free Chains.** We now consider the last contribution to the total concentration due to the free chains, eq 27c.

The general solution of eqs 33 and 34 can be written as

$$Z_f(n, z) = \sum_q K(q) \psi(q, z) \exp(-q^2 n) \quad (36)$$

where the eigenfunctions  $\psi(q, z)$  satisfy the eigenvalue equation

$$-[\psi(q, z)]'' + U(z)\psi(q, z) = q^2 \psi(q, z); \quad \psi(q, 0) = 0 \quad (37)$$

and

$$K(q) = \int \psi(q, z) dz$$

Here, in the free chains problem, only the continuous spectrum is involved. The free chain partition function  $Z_f$  is also equal to the second term in eq 20; however, the functions  $\psi(q, z)$  and  $K(q)$  in eq 20 and in eq 36 are

different: we have chosen here a boundary condition on the wall which is more natural for free chains. Let us define

$$\psi_f(z) = \psi(0, z) / \psi(0, \infty)$$

The free chain order parameter  $\psi_f(z)$  tends to 1 for  $z \rightarrow \infty$ , and we call  $\lambda_f$  the characteristic scale corresponding to the region where  $\psi_f$  is appreciably different from 1. We assume now that  $\lambda_f$  is much smaller than the chain size ( $\lambda_f \ll R = N^{1/2}$ ); we shall see below that this assumption is valid in most of the regimes, where  $\lambda_f$  is of the order of the cutoff tail size  $\lambda = n_c^{1/2} = \epsilon^{-1/2}$  ( $\lambda \ll R$ ). One can then show that for  $n \gg \tilde{n} = \lambda^2$ , the right hand side of eq 36 is dominated by the first term (with  $q = 0$ ) which is exactly equal to  $\psi_f(z)$ ; we thus write

$$Z_f(n, z) = \psi_f(z) + \delta Z_f(n, z) \quad (38)$$

where  $\delta Z_f \ll \psi_f$  if  $n \gg \tilde{n} = \lambda_f^2$ . The free chain concentration, eq 27c, can thus be written as

$$\phi_f(z) = \frac{\phi_0}{N} \left\{ N \psi_f^2(z) + 2 \psi_f(z) \varphi_f(z) + \int_0^N \delta Z_f(n, z) \delta Z_f(N-n, z) \, dn \right\} \quad (39)$$

where

$$\varphi_f(z) = \int_0^N \delta Z_f(n, z) \, dn \quad (40)$$

The last term in curly brackets in the right hand side of eq 39 can be neglected since  $\tilde{n} \ll N$  so that the integrand is always small.

The function  $\delta Z_f(n, z) \equiv Z_f(n, z) - \psi_f(z)$  still satisfies the "Schrödinger" equation

$$\frac{\partial \delta Z_f}{\partial n} = \delta Z_f' - U \delta Z_f; \quad \delta Z_f(n, 0) = 0 \quad (41)$$

so that

$$-\varphi_f'' + U \varphi_f = \delta Z_f(0, z) - \delta Z_f(N, z); \quad \varphi_f(0) = 0$$

When  $n$  goes to zero, the partition function  $\delta Z_f(n, z)$  is such that  $\delta Z_f(0, z) = Z_f(0, z) - \psi_f(z) = 1 - \psi_f(z)$ ; in the limit of high molecular weight  $\delta Z_f(N, z)$  is negligible. In addition it is clear that  $\varphi_f(\infty) = 0$ . We therefore obtain the following set of equations for the free chains:

$$\phi_f(z) = \phi_0 \left\{ \psi_f^2(z) + \frac{2}{N} \psi_f(z) \varphi_f(z) \right\} \quad (42)$$

$$-\psi_f'' + U \psi_f = 0; \quad \psi_f(0) = 0; \quad \psi_f(\infty) = 1 \quad (43)$$

$$-\varphi_f'' + U \varphi_f = 1 - \psi_f; \quad \varphi_f(0) = 0; \quad \varphi_f(\infty) = 0 \quad (44)$$

The first term in curly brackets in eq 42 corresponds to the contribution of the central parts of the free chains, whereas the second term corresponds to the end parts.

The set of eqs 28, 30, 35, 29, 42–44, and 25 completely defines the concentration profiles for loops, tails, and free chains for a given potential  $U(z)$ . In the adsorption

problem, the mean field potential  $U(z)$  is defined self-consistently:

$$U(z) = \phi - \phi_0 = \phi_l + \phi_t + \phi_f - \phi_0 \quad (45)$$

#### IV. Dilute Solution

**A. Extremely Dilute Solution Limit.** In this section we study the adsorption from a dilute solution and we assume that the bulk volume fraction  $\phi_0$  is extremely small ( $\phi_0 \ll 1/N$ ) so that both the concentration of free chains,  $\phi_f$ , and the bulk concentration can be neglected. [We always assume that the chains are long enough, so that  $N \gg b^2$ .] In the regime where the free chains can be neglected, there exists a first integral to the equations obtained in the previous section

$$(\psi')^2 + B \psi' \varphi' + \rho - \frac{1}{2}(\phi - \phi_0)^2 - \epsilon(\phi - \phi_0) = 0 \quad (46)$$

Let us first consider the region  $z \ll \lambda$ , where  $\lambda = 1/\sqrt{\epsilon}$  is the thickness of the adsorbed layer (the cutoff length). In this regime, the molecular potential  $U$  is much larger than  $\epsilon$  so that we can rewrite the basic eqs 28, 30, 28, and 35 neglecting  $\epsilon$  as

$$-\psi'' + U \psi = 0; \quad \psi'/\psi|_{z=0} = -1/b \quad (47a)$$

$$-\varphi'' + U \varphi = 1; \quad \varphi|_{z=0} = 0 \quad (47b)$$

$$U = \phi = \phi_l + \phi_t = \psi^2 + B \psi \varphi \quad (47c)$$

We first take the limit  $b \rightarrow 0$  and rescale the two functions  $\psi$  and  $\varphi$  and the unit length

$$\psi(z) = \frac{1}{l} \tilde{\psi}(z/l); \quad \varphi(z) = l^2 \tilde{\varphi}(z/l); \quad U(z) = \frac{1}{l^2} \tilde{U}(z/l)$$

where the crossover length  $l$  is defined as

$$l^2 = \frac{1}{B} \equiv \frac{NK}{2\Gamma} \quad (48)$$

Equations 47a–47c then read

$$-\tilde{\psi}'' + (\tilde{\psi}^2 + \tilde{\psi} \tilde{\varphi}) \tilde{\psi} = 0; \quad \tilde{\psi}(0) = \infty \quad (49a)$$

$$-\tilde{\varphi}'' + (\tilde{\psi}^2 + \tilde{\psi} \tilde{\varphi}) \tilde{\varphi} = 1; \quad \tilde{\varphi}(0) = 0 \quad (49b)$$

The universal functions  $\tilde{\psi}$  and  $\tilde{\varphi}$  satisfying eqs 49a and 49b have the following asymptotic behavior

$$\tilde{\psi}(\zeta) = \frac{\sqrt{2}}{\zeta}; \quad \tilde{\varphi}(\zeta) = \frac{1}{3} \zeta^2 \ln\left(\frac{1}{\zeta}\right) \quad \zeta \ll 1 \quad (50a)$$

$$\tilde{\psi}(\zeta) = \frac{360}{\zeta^4}; \quad \tilde{\varphi}(\zeta) = \frac{\zeta^2}{18} \quad \zeta \gg 1 \quad (50b)$$

The proper boundary conditions for the concentration profile can now be satisfied simply by changing  $z$  to  $z + b$  with a relative error of order  $b^2/N$  which is negligible everywhere. Thus  $\psi(z) = (1/l) \tilde{\psi}((z + b)/l)$  and the amplitude  $K$  is equal to

$$K = \int \psi(z) \, dz = \int_{b/l}^{\infty} \tilde{\psi}(\zeta) \, d\zeta \approx 2^{1/2} \ln(l/b) \quad (51)$$

The total adsorbance is then

$$\Gamma = \int \phi(z) \, dz \approx 2/b \quad (52)$$

**Table 1.** Concentration Profiles for  $\phi_0 \ll 1/N^a$ 

regime	type	$\phi_l$	$\phi_t$	$\phi_f$	$U$
$\lambda \ll z \ll D$	TH	$\sim \frac{(z^*)^6}{\lambda^8} e^{-2z/\lambda}$	$\sim \frac{1}{\lambda^2} e^{-z/\lambda}$	$\phi_0 P(z)$	$\phi_t + \phi_f - \phi_0$
$z^* \ll z \ll \lambda$	TE	$\frac{1800(z^*)^6}{z^8}$	$\frac{20}{z^2}$	$\sim \phi_0 \frac{z^7}{R^3 \lambda^4} \left(1 + \frac{z^3 R}{\lambda^4}\right)$	$\phi_t$
$b \ll z \ll z^*$	LE	$\frac{2}{z^2}$	$\frac{4z}{(z^*)^3} \ln\left(\frac{z^*}{z}\right)$	$\sim \phi_0 \frac{z^4 (z^*)^3}{R^3 \lambda^4} \ln\left(\frac{z^*}{z}\right)$	$\phi_l$

<sup>a</sup> The first letter in "type" is T (adsorbance is dominated by tails) or L (dominated by loops); the second letter is H (hairpin penetration of free chains) or E (end-penetration of free chains). Here  $z^* = [Nb \ln(N/b^2)]^{1/3}$ .

Note that the total adsorbed amount in this regime is dominated by short loops with a size  $z \sim b \ll l$  and is thus close to that predicted in the limit  $N \rightarrow \infty$  in the classical ground state dominance approximation (eq 11),  $\Gamma_0 = 2/b$ . The crossover length  $l$  is obtained from eqs 48, 51, and 52

$$l \simeq \frac{z^*}{2^{1/2} 3^{1/3}}, \quad z^* \equiv \left[ Nb \ln\left(\frac{N}{b^2}\right) \right]^{1/3} \quad (53)$$

The chain end point concentration is related to the order parameter  $\psi$  by eqs 24, 25, and 31

$$\rho_a(z) = \frac{2\Gamma}{NK} \psi(z) \quad (54)$$

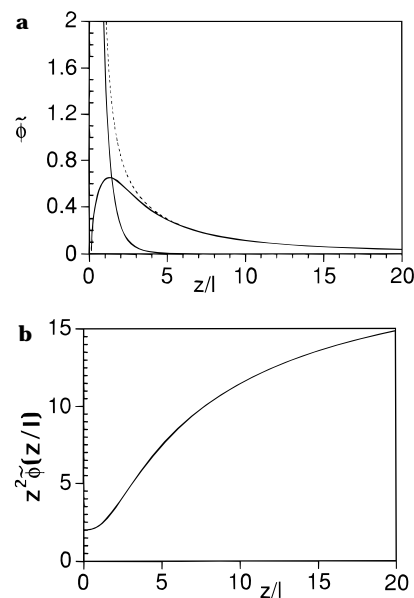
Therefore in the dilute solution regime, the chain end concentration is  $\rho(z) = \rho_a(z) = [4/bN \ln(l/b)](1/l)\tilde{\psi}((z+b)/l)$ .

The concentrations of monomers belonging to tails and loops are  $\phi_l(z) \simeq (1/P)\tilde{\phi}_l((z+b)/l)$  and  $\phi_t(z) \simeq (1/P)\tilde{\phi}_t((z+b)/l)$ , where  $\tilde{\phi}_l(\zeta) = \tilde{\psi}^2(\zeta)$  and  $\tilde{\phi}_t(\zeta) = \tilde{\psi}(\zeta)\tilde{\varphi}(\zeta)$ ; the asymptotic behaviors of these functions are given in Table 1. The results are in agreement with eqs 16a and 16b previously obtained by scaling arguments: in the region  $z \ll z^*$  the concentration is dominated by loops and the classical law, eq 11, is nearly valid; in the region  $z \gg z^*$  tails give the dominant contribution to the concentration; in the region  $z \sim z^*$  the tail concentration reaches a maximum. The scaling dependence of the total concentration  $\phi (=U)$  is the same in both regimes ( $z \ll z^*$ ,  $z \gg z^*$ ),  $\phi \sim 1/z^2$ ; however, the prefactor is larger by a factor of 10 in the region  $z \gg z^*$ . The universal concentration profiles  $\tilde{\phi}_l(\zeta)$  and  $\tilde{\phi}_t(\zeta)$  and  $\tilde{\phi} = \tilde{\phi}_l + \tilde{\phi}_t$  obtained numerically are shown in Figure 1. Note that the crossover regime  $z \sim z^*$  where neither of the asymptotic forms of  $\phi$  are quantitatively accurate is rather broad, corresponding approximately to  $z^* < z < 10z^*$ . The structure is clearly dominated by short loops ( $z \sim b$ ) created by adsorbed chains close to the wall, large loops being much less probable. On the other hand the tails are effectively expelled from the wall to a distance  $z \sim z^* \gg b$ , the maximum of  $\phi_t$  corresponding to  $z = z_{\max} = 0.63z^*$ .

We now discuss the cutoff region  $z \gtrsim \lambda$  where the molecular field  $U$  becomes comparable to  $\epsilon$ . The bound state energy  $\epsilon$  can be calculated from eqs 25, 51, and 52:

$$\epsilon \simeq \frac{1}{N} \ln\left(\frac{1}{\phi_0 b^2}\right) \quad (55)$$

where we have ignored a logarithmic factor in the argument of the logarithm. Note that  $\epsilon N \gg 1$  (if  $\phi_0$  is small) and that  $\lambda = 1/\sqrt{\epsilon}$  is smaller than the radius  $R$



**Figure 1.** (a) Universal concentration profiles for loops ( $\tilde{\phi}_l$ ), tails ( $\tilde{\phi}_t$ ), and total concentration  $\tilde{\phi} = \tilde{\phi}_l + \tilde{\phi}_t$ ;  $\tilde{\phi}_l$ ,  $\tilde{\phi}_t$ ,  $\tilde{\phi}$  vs  $z/l$  (dashed line total concentration, the tail concentration vanishes at the origin, the loop concentration diverges); (b)  $\tilde{\phi}(z)l^2$  vs  $z/l$ .

$= \sqrt{N}$  but is larger than the crossover length  $z^* \sim (Nb)^{1/3}$  in the asymptotic limit  $N \rightarrow \infty$ .

In the region  $z \sim \lambda \gg z^*$  the loop contribution to the total concentration can be neglected and thus the system of basic equations can be rewritten as

$$-\psi''_\lambda + (\varphi_\lambda \psi_\lambda + 1)\psi_\lambda = 0; \quad \psi_\lambda(0) = \infty \quad (56a)$$

$$-\psi''_\lambda + (\varphi_\lambda \psi_\lambda + 1)\varphi_\lambda = 1; \quad \varphi_\lambda(0) = 0 \quad (56b)$$

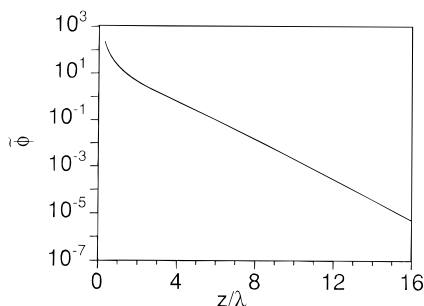
where we have defined  $\varphi(z) = \lambda^2 \varphi_\lambda(z/\lambda)$  and  $\psi(z) = (1/B\lambda^4)\psi_\lambda(z/\lambda)$ . These functions have the following asymptotic behaviors:

$$\psi_\lambda(\zeta) = \frac{360}{\zeta^4}; \quad \varphi_\lambda(\zeta) = \frac{\zeta^2}{18} \quad \zeta \ll 1 \quad (57a)$$

$$\psi_\lambda(\zeta) = \text{const exp}(-\zeta); \quad \varphi_\lambda(\zeta) = 1 \quad \zeta \gg 1 \quad (57b)$$

Equation 57a matches smoothly to eqs 50b, as expected. The concentration profiles  $\phi_l$  and  $\phi_t$  can be found from the general eqs 28 and 30. The numerical solution for the reduced total concentration,  $\phi_\lambda(\zeta) = \psi_\lambda(\zeta)\varphi_\lambda(\zeta)$  is shown in Figure 2.

The asymptotic behaviors for  $z \gg \lambda$  are also given in Table 1. Both  $\phi_l$  and  $\phi_t$  decay exponentially in this region, the decay length being  $\lambda$  for the tail concentra-



**Figure 2.** Reduced total concentration profile in the cutoff region  $z \sim \lambda$ :  $\phi_i(\xi)$  vs  $\xi = z/\lambda$ .

tion and  $\lambda/2$  for the loop concentration. The asymptotic variation of the concentration in the region  $z \gg \lambda$  is

$$\phi(z) \approx \phi_t(z) \sim \epsilon \exp(-z/\lambda) \quad (58)$$

so that in the cutoff region (for  $z \sim \lambda$ )  $\phi \approx \phi_t \sim \epsilon$ .

Let us now consider the variation of the adsorbance  $\Gamma$  with molecular weight. As already mentioned, the dominant contribution to the adsorbance,  $\Gamma_0 = 2/b$  (see eq 52), comes from the region close to the wall  $z \sim b$ . As  $\Gamma_0$  does not depend on  $N$ , we need to consider corrections to eq 52. The two main subdominant contributions to  $\Gamma$  are coming from the regions  $z \sim z^*$  and  $z \sim \lambda$ :  $\Gamma = \Gamma_0 + \Gamma_1 + \Gamma_2$ , where  $\Gamma_1 = (1/\lambda) \int [\phi(\xi) - (2/\xi^2)] d\xi$  and  $\Gamma_2 = (1/\lambda) \int [\phi_i(\xi) - (20/\xi^2)] d\xi$ . A numerical estimate of the integrals leads to

$$\Gamma = \frac{2}{b} + 7.07(Nb)^{-1/3} \left[ \ln \frac{N}{b^2} \right]^{-1/3} - 7.24N^{-1/2} \left[ \ln \frac{1}{\phi_0 b^2} \right]^{1/2} \quad (59)$$

The first correction is positive, giving rise to a decrease of  $\Gamma$  with  $N$ , whereas the second correction gives rise to an increase of  $\Gamma$  with the molecular weight. The adsorbance has thus a nonmonotonic variation with molecular weight. In the limit  $N \rightarrow \infty$  the second correction is negligible and for large  $N$  we predict that  $\Gamma$  slightly decreases with molecular weight. Although this anomalous dependence<sup>1</sup> is counterintuitive, it can be explained in a simple way: the structure of the adsorbed layers depends on molecular weight mostly via the dependence of the number of tails (per unit area) which decreases as  $1/N$ . As shown above, the tails are expelled from the wall and contribute appreciably to the total concentration in the region  $z \gtrsim z^*$ . On the other hand the structure of the adsorbed layer near the surface is insensitive to  $N$  (if  $N$  is large), as it is governed by a balance between the attraction of short loops to the wall and their mutual repulsions. Therefore the variation of the adsorbance with molecular weight comes from the tail contribution and the adsorbance decreases with molecular weight.

Using eq 59, we estimate that the maximum of  $\Gamma$  is reached when  $N = N_c \approx 1.3 \times 10^7 b^2$ : for  $N < N_c$  we predict a normal increase of  $\Gamma$  with  $N$ . Therefore the anomalous regime considered above is probably only of academic interest since  $N_c$  is too large to be reached in experiments or computer simulations (note that in general  $b > 1$ , i.e. the extrapolation length is longer than the statistical length divided by  $\sqrt{6}$ ).

Another interesting question is the variation of the concentration at the adsorbing wall,  $\phi(0)$ , with  $N$ . Using the general conservation law (46) we obtain

$$\phi(0) \approx \frac{2}{b^2} - 2\epsilon \approx \frac{2}{b^2} - \frac{2}{N} \ln \left( \frac{1}{\phi_0 b^2} \right)$$

Thus  $\phi(0)$  is always increasing with molecular weight as expected. Note that an increase of  $\phi(0)$  with  $N$  is dictated by general thermodynamic rules provided that longer chains always tend to substitute shorter ones in the adsorbed layer at equilibrium. However, there is no similar rule for the adsorbance  $\Gamma$ .

**B. Free Chains: Depletion.** In our previous analysis, the concentration of free chains has been neglected; we now discuss explicitly the role of the free chains in the limit where  $\phi_0 \ll 1/N$ . The contribution of free chains to the concentration is negligible at the edge of the adsorbed layer ( $z \sim \lambda$ ) where  $\phi \sim \epsilon \gg \phi_0$ , and also in the regions closer to the wall. On the other hand for  $z \gg \lambda$  the interaction between monomers is negligible since  $U_{\text{int}}N \sim \phi_0 N \ll 1$ . Therefore the typical scale corresponding to the free chains concentration profile is of the order of the Gaussian radius  $R = \sqrt{N}$ ; i.e. much larger than  $\lambda$ . The free chains must feel the wall and the excluded volume repulsion of the adsorbed layer of thickness  $\lambda \ll R$  as a virtually impenetrable hard surface. At a scale  $R$ , the concentration of free chains is thus nearly the same as that of ideal (noninteracting) chains near a hard wall. [Of course these conclusions are supported by the analysis of the basic "free chain" equations (42)–(44), which are qualitatively valid in the present regime. The typical length scale  $\lambda_f$  is not much smaller than  $R$ , as required for these equations to be strictly valid; rather it is of order  $R$ . Note that the end contribution (second term in curly brackets in eq 42) can be neglected in the region  $z > \lambda$ .] This distribution is well-known and can be easily found using the image charge method:<sup>16</sup>

$$\phi_f(z) = \phi_0 P(z/R) \quad (60)$$

where  $P(x) = 1 - 8i^2 \text{erfc}(x/2) + 4i^2 \text{erfc}(x)$  has the asymptotic behaviors  $P(x) \approx x^2/2$  for  $x \ll 1$  and  $P(x) \approx 1 - (16/\pi)x^{-3} \exp(-x^2/4)$  for  $x \gg 1$ . The function  $i^n \text{erfc}(x)$  is a repeated integral of the error function defined in ref 20:  $i^{n+1} \text{erfc}(x) = \int_x^\infty i^n \text{erfc}(x) dx$ ;  $i^0 \text{erfc}(x) = \text{erfc}(x) = (2/\sqrt{\pi}) \int_x^\infty \exp(-x^2) dx$ . Therefore  $\phi_f \approx \phi_0$  for  $z \gg R$ , and  $\phi_f \approx \phi_0 z^2/2N$  for  $\lambda \ll z \ll R$ , so that

$$\phi_f(\lambda) \sim \frac{\phi_0}{\epsilon N} \quad (61)$$

At the edge of the adsorbed layer, the concentration of free chains is small,  $\phi_f(\lambda) \ll \phi_0 \ll \phi_a(\lambda) \sim \epsilon$ .

The total concentration profile for  $z \gg \lambda$  is then

$$\phi(z) = \phi_a(z) + \phi_f(z) = \text{const } \epsilon \exp(-z/\lambda) + \phi_0 P(z/R) \quad (62)$$

In the region  $z \gg \lambda$  the total concentration is smaller than  $\phi_0$ : this is a depletion region. The relative depth of the depletion  $(\phi_0 - \phi_{\text{min}})/\phi_0$  (where  $\phi_{\text{min}}$  is the minimum of the concentration) depends on  $\phi_0$ . For  $\phi_0 \sim 1/N$  the depletion is quite pronounced; the relative depth is close to unity:  $\phi_{\text{min}}/\phi_0 \sim 1/\ln N$ . The distance corresponding to the minimum,  $z_{\text{min}}$ , is of the order of the coil size:  $z_{\text{min}} \sim R/\sqrt{\ln N}$ . However, as the bulk concentration decreases (in the region  $\phi_0 \ll 1/N$ ), the depletion depth rapidly decreases and tends to zero; the

position of the minimum,  $z_{\min}$ , in this regime shifts to the region  $z \gg R$ :  $z_{\min} \approx D \equiv 2N\sqrt{\epsilon}$ .

The total concentration is very close to  $\phi_0$  in the region  $z \gg R$ ; in this region both  $\phi_a(z)$  defined by eq 58 and  $\delta(z) \equiv 1 - \phi_f(z)/\phi_0$  are exponentially small:

$$\phi_a(z) = \text{const } \epsilon \exp(-z/\lambda); \quad \delta(z) = 1 - P(z/R) \quad (63)$$

We briefly discuss now the rather academic but still interesting question of the validity of eqs 63. These equations are in fact valid only if  $z$  is smaller than  $D = 2N\sqrt{\epsilon}$ . The exponential decay of the concentration of adsorbed chains  $\phi_a$  can be rederived by the following simple argument. An adsorbed chain with one end point at the distance  $z \gg \lambda$  from the wall consists of two parts: an adsorbed part (a train) of  $N - n$  monomers and a rather long tail of  $n$  monomers and of length  $z$ . The number  $n$  is determined by the balance between the adsorption energy  $-\epsilon(N - n)$  ( $-\epsilon$  per monomer of the train) and the elastic energy of the stretched tail which is  $z^2/(4n)$  [as far as we are aware, arguments of this type applied to a different problem were first published by Johner et al.<sup>21</sup>]; the result is  $n = z/(2\sqrt{\epsilon})$  so that the effective free energy of the chain is  $F_1(z) = -\epsilon N + z\sqrt{\epsilon}$ . Therefore, the end distribution is

$$\rho(z) = \text{const } \phi_0 \exp(-F_1(z)) = \text{const } \phi_0 \exp(\epsilon N) \exp(-z/\lambda) \quad (64)$$

Note that  $z/n$  is constant (independent of  $z$ ), so that the tails are nearly uniformly stretched. Their statistics can be described in terms of Pincus blobs<sup>22</sup> of size  $\lambda$  containing  $g = n_c = 1/\epsilon$  monomers. The total concentration of adsorbed monomers at a distance  $z$  is proportional to  $\rho(z)$ :  $\phi_a(z) \sim g\rho(z)$ . Adsorbing  $g$  in the constant in eq 64 gives

$$\phi_a(z) = \text{const } \phi_0 \exp(\epsilon N) \exp(-z/\lambda) \quad (65)$$

in agreement with eqs 58 and 55.

Equation 65 can be valid only if  $n < N$ , i.e. for  $z < D = 2N\sqrt{\epsilon}$ . In the region  $z > D$  the train part is negligible and the chain free energy is essentially due to the stretching of the tail (=of the whole chain):  $F_1(z) = z^2/(4N)$ . Thus, keeping only the exponential terms, we write the concentration of adsorbed chains

$$\ln(\phi_a(z)/\phi_0) = \begin{cases} \epsilon N - z\sqrt{\epsilon}, & z < D \\ -\frac{z^2}{4N} & z > D \end{cases} \quad (66)$$

The correction to the concentration of free chains,  $\delta(z)$ , is determined both by the interaction with the adsorbed layer and the wall and by the excluded volume interaction with other monomers outside the adsorbed layer (i.e. in the region  $z > \lambda$ ). This correction can be calculated by perturbation theory (the details being omitted here). For  $z < D$ , it is the interaction with the wall which is dominant so that eq 63 is valid. For  $z > D$  the situation is opposite; if  $D < z < 2D$  then the critical chain conformation (giving rise to a dominant contribution to  $\delta(z)$ ) is a nearly uniformly stretched chain with one end at the distance  $z - D$  and the other end at the distance  $z$  from the wall; if  $z > 2D$  then the critical conformation implies that the ends are at distances  $z/2$  and  $z$ . The final results (with the same

accuracy as in eq 66) are

$$\ln(\delta(z)) = \begin{cases} -\frac{z^2}{4N} & z < D \\ N\epsilon - z\sqrt{\epsilon}, & D < z < 2D \\ -\epsilon N - \frac{z^2}{8N} & z > 2D \end{cases} \quad (67)$$

Comparing eqs 66 and 67, we see that  $\phi_a(z)$  is much larger than  $\phi_0 - \phi_f(z)$  if  $z < D$  and vice versa if  $z > D$ ; thus these equations confirm that the minimum of  $\phi(z)$  is located at  $z = D$ .

**C. Free Chains: Penetration.** In the region  $z < \lambda$ , the free chain concentration  $\phi_f$  is much smaller than the adsorbed chain concentration  $\phi_a$ . The profile  $\phi_f(z)$  is thus related to the probability of penetration of free chains into the adsorbed layer. The study of this profile is important for example to understand the dynamics of adsorption.

We will consider only the scaling behavior of  $\phi_f$ , ignoring numerical prefactors. For that purpose we can still use eqs 42–44. Note that in the region  $z \ll \lambda$  the molecular field  $U(z)$  is much larger than  $\epsilon$ , which can be neglected. Also, in this region, the free chain order parameter is small,  $\psi_f(z) \ll 1$ . Therefore the differential equations (35) and (44) for the two functions  $\varphi(z)$  and  $\varphi_f(z)$  are nearly identical with similar boundary conditions at  $z = 0$ . Thus

$$\varphi(z) \approx \varphi_f(z) \quad (68)$$

(the boundary conditions at  $z \rightarrow \infty$  are irrelevant for the behavior of these functions in this region). The differential equations (29) and (43) for  $\psi(z)$  and  $\psi_f(z)$  are also nearly identical. However, the boundary conditions (at  $z = 0$ ) are different. Yet the structure of the differential equation implies a general relation between any two of its solutions, which in terms of  $\psi$  and  $\psi_f$  can be written as

$$\psi_f(z) = C_1 \psi(z) \int_0^z \frac{dz}{\psi^2(z)} \quad (69)$$

The boundary condition  $\psi_f(0) = 0$  has been taken into account in this relation.

The whole concentration profile of free chains  $\phi_f(z)$  can be found using eqs 68 and 69, and the results, eqs 50a, 50b, 57a, and 57b, for the functions  $\psi(z)$  and  $\varphi(z)$ . The integration constant is fixed by matching  $\phi_f$  for  $z \sim \lambda$  with the profile obtained at large distances, eq 61. The asymptotic behaviors in the different regimes (including  $z^* \ll z \ll \lambda$  and  $b \ll z \ll z^*$ ) are given in Table 1. Note that in the region  $z \sim \lambda$  it is the central parts of the chains that give the dominant contribution to  $\phi_f$  (this corresponds to what was called hairpin penetration in ref 7). It means that the first term in the curly brackets of eq 42 dominates. This situation persists in a rather narrow region  $\lambda \gtrsim z \gtrsim z_1 = \lambda^{4/3}/R^{1/3}$ , where  $\phi_f(z) \sim \phi_0(z^{10}/R^2\lambda^8)$ . For  $z \ll z_1$  the situation is opposite,  $\phi_f$  is dominated by end penetration (formally corresponding to the dominance of the second term in eq 42); we obtain  $\phi_f \sim \phi_0(z^7/R^3\lambda^4)$  in the region  $z_1 \gg z \gg z^*$ , and  $\phi_f \sim \phi_0[(z^*)^3/R^3\lambda^4]z^4 \ln(z^*/z)$  closer to the wall, for  $z^* \gg z \gg b$ . Thus the adsorbed layer is not transparent to free chains; the permeability of the layer can be characterized by the ratio  $p_f = \phi_f(b)/\phi_0$ ; omitting log factors, we get  $p_f \sim (b/R)^5 \ll 1$ , so that the permeability is very low.

Table 2. Concentration Profiles for  $1/N \ll \phi_0 \ll \epsilon$ 

regime	type	$\phi_l$	$\phi_t$	$\phi_f$	$U$
$\lambda \ll z \ll D$	TH	$\sim \frac{(z^*)^6}{\lambda^8} e^{-2z/\lambda}$	$\sim \frac{1}{\lambda^2} e^{-z/\lambda}$	$\phi_0 \tanh^2\left(\frac{z}{2\zeta}\right)$	$\phi_t + \phi_f - \phi_0$
$z^* \ll z \ll \lambda$	TE	$\frac{1800(z^*)^6}{z^8}$	$\frac{20}{z^2}$	$\sim \phi_0 \frac{z^7}{R^2 \zeta \lambda^4} \left(1 + \frac{z^3 R^2}{\lambda^4 \zeta}\right)$	$\phi_t$
$b \ll z \ll z^*$	LE	$\frac{2}{z^2}$	$\frac{4z}{(z^*)^3} \ln\left(\frac{z^*}{z}\right)$	$\sim \phi_0 \frac{z^4 (z^*)^3}{R^2 \zeta \lambda^4} \ln\left(\frac{z^*}{z}\right)$	$\phi_l$

## V. Semidilute Regimes

In this section, we discuss the change in the structure of an adsorbed polymer layer when the bulk concentration increases from a dilute to a concentrated solution  $\phi_0 \gg \phi^* \sim 1/N$  which we call the semidilute range; the highest concentration in this regime corresponding to concentrated solutions is obtained at the end of this section. In the semidilute range, the concentration profiles  $\phi_l$ ,  $\phi_t$ , and  $\phi_f$  are quantitatively determined by the set of eqs 28, 30, 35, 29, and 42–44 obtained in section 3. Thus for any particular concentration, the profiles can be found as a numerical solution of these equations. The free chain concentration can be also found using eqs 68 and 69 in the region  $z \ll \lambda$ . For  $z \gtrsim \lambda$  the second term in eq 42, containing  $\phi_f$  and giving the end contribution, is never important. We describe here the various possible adsorption profiles and we focus on analytical (rather than numerical) solutions of the basic equations to find asymptotic behaviors.

**A. Vicinity of  $\phi^*$ ,  $1/N \ll \phi_0 \ll \epsilon$ .** The characteristics of the adsorbed layer in this rather narrow regime are very similar to those of dilute solutions described in the previous section for  $\phi_0 < 1/N$ . However, there is a slight difference in the distribution of free chains. For  $z \gg \lambda$  the adsorbed layer plays the role of an effectively impenetrable wall for free chains (as in a more dilute regime); however, the concentration profile, eq 60, cannot be used here since the bulk solution is semidilute: the bulk correlation length,  $\xi = 1/\sqrt{2\phi_0}$  (see eq 9), is smaller than  $R$ . The behavior of a semidilute solution near a hard wall is well-known;<sup>13,23</sup> it is governed by the equations

$$-\psi_f'' + U\psi_f = 0; \quad U = \phi - \phi_0; \quad \phi = \phi_0 \psi_f^2; \\ \psi_f(0) = 0; \quad \psi_f(\infty) = 1 \quad (70)$$

(which can be also derived from eqs 42–44). The solution is  $\psi_f(z) = \tanh(z/2\xi)$ , and the free chain concentration is

$$\phi_f(z) = \phi_0 \tanh^2\left(\frac{z}{2\xi}\right) \quad z \gg \lambda \quad (71)$$

(note that  $\xi \gg \lambda$ ).

The total concentration  $\phi = \phi_a + \phi_f \simeq \phi_t + \phi_f$  in the region  $\lambda \ll z \ll \xi$  is then

$$\phi(z) \simeq \text{const } \epsilon \exp(-z/\lambda) + \phi_0 \frac{z^2}{4\xi^2} \quad (72)$$

This shows a pronounced depletion; the concentration reaches a minimum value,  $\phi_{\min} \ll \phi_0$ , in this region. Note that the relative depth of the concentration hole ( $\phi_0 -$

$\phi_{\min}$ )/ $\phi_0$  is close to unity for  $\phi_0 \ll \epsilon$ ; for  $\phi_0 \sim \epsilon$  we predict that  $\phi_{\min} \sim \phi_0/2$ .

The change of the profile given by eq 71 also induces some small changes of the profile  $\phi_f(z)$  inside the adsorbed layer, for  $z \ll \lambda$ . The equations giving the concentration profiles and the mean field potential,  $U$ , at various distances from the wall are collected in Table 2.

**B. Semidilute-Tails Regime,  $\epsilon \ll \phi_0 \ll \phi_1$ .** When the concentration is increased, the semidilute-tails regime is reached where the correlation length is shorter than the cutoff length  $\lambda$ , but longer than  $z^*$  ( $\lambda \gg \xi \gg z^*$ ),

$$\epsilon \ll \phi_0 \ll \phi_1 = (bN)^{-2/3} \quad (73)$$

The scale  $z^*$  defined by the condition  $\phi_l(z^*) \sim \phi_t(z^*)$  and the bound state energy  $\epsilon$  are determined by eqs 53 and 55 which remain valid throughout the semidilute-tails regime. The bound state energy  $\epsilon$  is slightly decreasing with the bulk concentration,  $\epsilon/N \simeq \ln(1/\phi_0 b^2)$ , nevertheless the basic condition (19) is fulfilled.

The main results for this regime (which can be obtained just in the same way as for more dilute solutions) are shown in Table 3. Note a new regime  $\xi \ll z \ll \lambda$ , where the total concentration is close to the bulk limit,  $\phi_0$ , but is still dominated by tails, the contribution of loops and free chains being negligible (the concentration of monomers belonging to loops decreases as  $\phi_l \propto z^{-4}$  in this region). Note also that the depletion is quite shallow in the semidilute-tails regime (73); the total concentration and the molecular potential,  $U$ , both show a minimum at  $z \sim \lambda$ ; the depth of the minimum,  $\phi_0 - \phi_{\min} \sim \epsilon$ , is small in comparison with  $\phi_0$ . The concentrations due to free chains and adsorbed chains are comparable in the cutoff region:  $\phi_a \equiv \phi_t + \phi_l \sim \phi_f \sim \phi_0/2$  for  $z/\lambda \sim 1$ . As  $z/\lambda$  is decreased, the adsorbed chain contribution  $\phi_a$  tends to  $\phi_0$  (we assume that still  $z \gg \xi$ ), and the concentration of free chains rapidly decreases.

The permeability of the adsorbed layer,  $p_f = \phi_f(b)/\phi_0 \sim (b^5/R^3)\phi_0$  is increasing with the bulk concentration, but it remains small throughout this regime.

Using the results shown in Table 3, it is easy to check that the adsorbance  $\Gamma$  is always close to  $\Gamma_0 = 2/b$ . Thus the dominant contribution to  $\Gamma$  comes from a thin layer close to the wall, the characteristic thickness of the layer being of order  $b$ .

**C. Semidilute-Loops Region,  $\phi_1 \ll \phi_0 \ll \phi_2$ .** In the semidilute-loops region, the bulk correlation length,  $\xi$ , is shorter than  $z^*$ , but still the basic inequality (19) is fulfilled. The first condition imposes  $\phi_0 > \phi_1$ . The second condition is equivalent to the requirement that the adsorbance is dominated by loops (that is “trains” are much longer than “tails”; see section 3). We must

**Table 3. Concentration Profiles for  $\epsilon \ll \phi_0 \ll \phi_1 \equiv 1/(bN)^{3/2}$** 

regime	type	$\phi_l$	$\phi_t$	$\phi_f$	$U$
$\lambda \ll z \ll D$	TH	$\sim \phi_0 \frac{(z^*)^6}{\lambda^4 \xi^2} e^{-2z/\lambda}$	$\sim \phi_0 e^{-z/\lambda}$	$\phi_0 - \phi_t + U$	$-\left(\frac{\xi}{\lambda}\right)^2 \phi_t$
$\xi \ll z \ll \lambda$	TE	$\frac{1}{18} \phi_0 \frac{(z^*)^6}{\lambda^4 \xi^2}$	$\phi_0$	$\sim \phi_0 \frac{z^5}{R^2 \lambda^3} \left(1 + \frac{zR^2}{\lambda^3}\right)$	$\frac{6}{z^2}$
$z^* \ll z \ll \xi$	TE	$\frac{1800(z^*)^6}{z^8}$	$\frac{20}{z^2}$	$\sim \phi_0 \frac{z^7}{R^2 \xi^2 \lambda^3}$	$\frac{20}{z^2}$
$b \ll z \ll z^*$	LE	$\frac{2}{z^2}$	$\frac{4z}{(z^*)^3} \ln\left(\frac{z^*}{z}\right)$	$\sim \phi_0 \frac{z^4 (z^*)^3}{R^2 \xi^2 \lambda^3} \ln\left(\frac{z^*}{z}\right)$	$\frac{2}{z^2}$

thus compare the contributions of loops and tails to the adsorbances  $\Gamma_l$  and  $\Gamma_t$ , respectively. The contribution of loops,  $\Gamma_l$ , is dominated by the short loops close to the wall, it is nearly equal to  $\Gamma_0 = 2/b$ . In order to estimate the tail contribution,  $\Gamma_t$ , we note that tails give a dominant contribution to the total concentration in the region  $z^* < z < \lambda$  since the free chains only slightly penetrate into the region  $z \ll \lambda$ . On the other hand the total concentration in the region  $z^* < z < \lambda$  is close to  $\phi_0$  since  $z^*$  is much larger than the bulk correlation length. Therefore  $\Gamma_t \sim (\lambda - z^*)\phi_0 \sim \lambda\phi_0$  (it is explicitly checked below that  $\lambda \gg z^*$ ).

Therefore the condition  $\Gamma_l \gg \Gamma_t$  can be written as  $2/b \gg \lambda\phi_0$ , or  $\phi_0 \ll 1/b\lambda$ ; the cutoff length,  $\lambda = 1/\sqrt{\epsilon}$ , is roughly of the order of the gyration radius  $R$ , and we finally get  $\phi_0 \ll \phi_2$  where

$$\phi_2 = \frac{1}{bN^{1/2}} \quad (74)$$

The concentration near the wall, for  $z \ll z^*$ , is dominated by short loops. Hence the results obtained from the classical ground state dominance approximation outlined in section 2 are valid in this region (see eq 10):

$$\phi(z) \simeq \phi_l(z) \simeq \phi_0 \coth^2\left(\frac{z}{2\xi} + \beta\right) \quad (75)$$

where  $\beta$  is defined in eq 9. The order parameter  $\psi(z)$  is close to  $\sqrt{\phi_0}$  in the region  $z > \xi$ .

We now consider the distributions of loops and tails in the region  $\xi \ll z \ll z^*$  more closely. The concentration profiles are governed by the basic differential equations (29) and (35), where  $\epsilon$  can be neglected in comparison with  $U$  (the condition  $U \gg \epsilon$  is verified below). Thus

$$-\psi'' + U\psi = 0; \quad U = \psi^2 + B\psi\varphi - \phi_0 \quad (76)$$

Instead of the second equation (35), it is convenient to use here the conservation equation (46) which is valid since the contribution of free chains is negligible in the region closer to the wall than the cutoff length,  $z^* \ll \lambda$ . Neglecting the last term (proportional to  $\epsilon$ ) in the left hand side of eq 46, we obtain

$$(\psi')^2 + B\psi'\varphi' + B\psi - \frac{1}{2}U^2 = 0 \quad (77)$$

As the order parameter  $\psi(z)$  is close to  $\sqrt{\phi_0}$ , we can write  $\psi(z) = \sqrt{\phi_0}[1 + \eta(z)]$ , where  $\eta(z)$  is small. The tail contribution  $\phi_t = B\psi\varphi$  can be also considered as a small perturbation ( $\phi_t \ll \phi_l \simeq \phi_0$ ). Up to leading order

in these perturbations,  $\eta$  and  $\phi_t/\phi_0$ , eqs 76 and 77 read

$$-\xi^2 \eta'' + \eta + \frac{1}{2f^2} \varphi = 0 \quad (78)$$

$$\phi_0 \left[ (\eta')^2 + \frac{1}{f^2} \eta' \varphi' \right] - \frac{\phi_0^2}{2} \left[ 2\eta + \frac{\varphi}{f} \right]^2 + B\sqrt{\phi_0} = 0 \quad (79)$$

where we define the length

$$l \equiv \frac{\phi_0^{1/4}}{B^{1/2}}$$

In the region  $z \gg \xi$  the first term in eq 78 can be neglected, so that  $\eta + \varphi/(2f) \simeq 0$ . Substituting this last equation into eq 79, we get  $\eta' \simeq -1/l$  and  $\varphi' \simeq 2l$ ; the boundary condition  $\varphi(0) = 0$  thus leads to

$$\varphi(z) \simeq 2lz, \quad \eta(z) \simeq -z/l \quad (80)$$

The contributions of tails and loops to the monomer concentration are

$$\phi_l(z) \simeq \phi_0[1 - 2z/l]; \quad \phi_t(z) \simeq 2\phi_0 z/l \quad (81)$$

Therefore  $\phi_t \sim \phi_l$  for  $z \sim l$ , so that the scale  $l$  must be identified with  $z^*$ :

$$z^* = l = \xi(\phi_0^{3/2} NK/\Gamma)^{1/2} \quad (82)$$

The molecular field  $U = \phi_l + \phi_t - \phi_0$  is nearly zero when  $\xi \ll z \ll z^*$ . Extending the perturbation expansion to higher orders, we obtain

$$U(z) \simeq \frac{3}{2} \left(\frac{1}{z^*}\right)^2 \left(1 - \frac{z}{z^*}\right) \quad (83)$$

The potential slightly decreases in this region and remains approximately constant. We also see that, indeed, the typical value  $U \sim 1/(z^*)^2$  is much larger than  $\epsilon = 1/\lambda^2$  because  $\lambda \gg z^*$ .

In the more distant region  $z^* \ll z \ll \lambda$ , the contribution of free chains to the total monomer density is still negligible. Here the functions  $\psi$  and  $\varphi$  and also the profiles  $\phi_l$ ,  $\phi_t$  are obtained directly from the basic equations (29) and (35). The results are

$$\varphi(z) = z^2/4; \quad \psi(z) = 4\sqrt{\phi_0} \left(\frac{z^*}{z}\right)^2 \quad (84)$$

$$\phi_t(z) \simeq \phi_0; \quad \phi_l(z) \simeq 16\phi_0 \left(\frac{z^*}{z}\right)^4; \quad U(z) \simeq \frac{6}{z^2} \quad (85)$$

**Table 4. Concentration Profiles for  $\phi_1 \ll \phi_0 \ll \phi_2 = 1/bN^{1/2}$ ; here  $z^* \sim \phi_0 Nb$** 

regime	type	$\phi_l$	$\phi_t$	$\phi_f$	$U$
$\lambda \ll z \ll D$	TH	$\sim \phi_0 \frac{(z^*)^4}{\lambda^4} e^{-2z/\lambda}$	$\sim \phi_0 e^{-z/\lambda}$	$\phi_0 - \phi_t + U$	$-\left(\frac{\xi}{\lambda}\right)^2 \phi_t$
$z^* \ll z \ll \lambda$	TE	$16\phi_0 \left(\frac{z^*}{z}\right)^4$	$\phi_0$	$\sim \phi_0 \frac{z^5}{R^2 \lambda^3} \left(1 + \frac{zR^2}{\lambda^3}\right)$	$\frac{6}{z^2}$
$\xi \ll z \ll z^*$	LE	$\phi_0 \left[1 - 2\frac{z}{z^*} + 3\left(\frac{\xi}{z^*}\right)^2\right]$	$2\phi_0 \frac{z}{z^*}$	$\sim \phi_0 \frac{z^2 (z^*)^3}{R^2 \lambda^3}$	$3\phi_0 \left(\frac{\xi}{z^*}\right)^2 \left(1 - \frac{z}{z^*}\right)$
$b \ll z \ll \xi$	LE	$\frac{2}{z^2}$	$\frac{2\phi_0 z}{3z^*}$	$\sim \phi_0 \frac{z^4 (z^*)^3}{R^2 \xi^2 \lambda^3}$	$\frac{2}{z^2}$

The crossover length  $z^*$  can now be estimated. The only unknown quantity in eq 82 is  $K = \int \psi(z) dz$ . The order parameter  $\psi(z)$  has the following asymptotic behavior

$$\psi(z) = \sqrt{\phi_0} \times \begin{cases} \frac{2\xi}{z} & b \ll z \ll \xi \\ 1 & \xi \ll z \ll z^* \\ \left(\frac{2z^*}{z}\right)^2 & z^* \ll z \ll \lambda \end{cases}$$

Therefore  $K \sim \sqrt{\phi_0} z^*$  and

$$z^* \sim N\phi_0 b \quad (86)$$

The bound state energy,  $\epsilon$ , is defined by eq 25 which gives with logarithmic accuracy

$$\epsilon \simeq \frac{4}{N} \ln \frac{R}{z^*} = \frac{4}{N} \ln \frac{\phi_2}{\phi_0} \quad (87)$$

Therefore the condition  $\epsilon N \gg 1$  is indeed satisfied in the region  $\phi_0 \ll \phi_2$ . One can also check directly that  $\lambda \gg z^*$ .

The tail contribution to the monomer density in the region  $b \ll z \leq \xi$  is  $\phi_t = B\psi\phi$ . The function  $\varphi$  is defined by eqs 35; in the region  $z \sim \xi$  we estimate  $\varphi \sim \xi z^*$  (see eq 80) and  $U \sim \phi \sim 1/\xi^2$ ; therefore  $U\varphi \sim z^*/\xi \gg 1$  so that 1 in the right hand side of the differential equation (35) can be neglected and

$$-\varphi'' + (U + \epsilon)\varphi \simeq 0 \quad (88)$$

Thus the differential equations for  $\psi$  and  $\varphi$  are identical and there is a relationship between these functions similar to eq 69:

$$\varphi(z) \simeq \text{const } \psi(z) \int_0^z \frac{dz}{\psi^2(z)} \quad (89)$$

One can easily check that  $\varphi(z)$  given by eq 89 is very close to the exact solution of eqs 35 in the whole region,  $b \ll z \ll z^*$ . Using eqs 89 and 8 we get

$$\phi_t(z) = \text{const } z f_t\left(\frac{z}{2\xi}\right);$$

$$f_t(x) = \frac{1}{\tanh(x)} \left[ \frac{1}{\tanh(x)} - \frac{1}{x} \right] \quad (90)$$

The unknown constant in the first eq 90 can be found by matching this equation with the second eq 81 in the region  $\xi \ll z \ll z^*$ . The final result valid in the

whole region  $b \ll z \ll z^*$  is

$$\phi_t(z) = \frac{2\phi_0 z}{z^*} f_t\left(\frac{z}{2\xi}\right) \quad (91)$$

All the asymptotic results for the monomer densities due to loops, tails, and free chains are collected in Table 4. Note that the behavior of tails and free chains in the cutoff region  $z \sim \lambda$  is nearly the same as for the more dilute regime  $\phi < \phi_1$ . In particular the total monomer concentration is slightly depleted in this region, the relative depth of the depletion being  $\sim \epsilon/\phi_0$ . The monomer density of free chains in the region  $z \ll \lambda$  is found using eqs 68 and 69. Note that as in the previous regime (for  $\phi < \phi_1$ ) the concentration  $\phi_f$  is dominated by end penetration for  $z < \lambda^3/R^2$ , i.e. almost everywhere inside the adsorbed layer. The penetration factor is  $p_f = \phi_f(b)/\phi_0 \sim (b^7 N^2/\lambda^3)\phi_0^4$ .

## VI. Concentrated Solution

**A. Asymptotic Limit of Infinite Chains.** In the previous section we have considered the semidilute regimes  $\phi_0 \ll \phi_2 = 1/b\sqrt{N}$  in the limit of strong adsorption where the binding energy per chain,  $\epsilon N$ , is large. We now turn to the concentrated regime  $\phi_0 \gg \phi_2$ , which is actually a regime of weak adsorption: the binding energy per chain is small,  $\epsilon N \ll 1$ , so that the bound state is unimportant.

At the boundary of the weak adsorption regime,  $\phi_0 \sim \phi_2$ , both the cutoff length  $\lambda$  and the length  $z^*$  are of the order of the Gaussian size:  $\lambda \sim z^* \sim R$  (eqs 68 and 69). The weak adsorption regime is thus characterized by a single large length scale, the gyration radius  $R$ . The other (shorter) relevant length scales are the bulk correlation length,  $\xi = 1/\sqrt{2\phi_0}$ , and the extrapolation length  $b$ .

In the region  $z \ll R$ , loops dominate and the standard mean field results obtained in the limit  $N \rightarrow \infty$  are applicable. In particular the total concentration is given by eq 10:

$$\phi^{(0)}(z) = \phi_0 \coth^2\left(\frac{z}{2\xi} + \beta\right) \quad (92)$$

for  $z \ll R$  ( $\beta$  is defined in eq 9), so that  $\phi$  is extremely close to  $\phi_0$  for  $z \gg \xi$ . Clearly, eq 92 is also valid in the region  $z \gtrsim R$ . The density of chain ends,  $\rho(z)$ , is proportional to  $\psi(z)$  given by eq 8. Taking into account the bulk value  $\rho = 2\phi_0/N$  we thus get

$$\rho^{(0)}(z) = \frac{2\phi_0}{N} \coth\left(\frac{z}{2\xi} + \beta\right) \quad (93)$$

**Table 5. Concentration Profiles for  $\phi_2 \ll \phi_0 \ll 1/b^2$** 

regime	type	$\phi_l$	$\phi_t$	$\phi_f$	$U$
$z \gg R$	TH	$\frac{\phi_0}{\sqrt{\pi}} \left(\frac{R}{z}\right)^3 \exp\left(-\frac{z^2}{R^2}\right)$	$\frac{16}{\sqrt{\pi}} \phi_0 \left(\frac{R}{z}\right)^3 \exp\left(-\frac{z^2}{4R^2}\right)$	$\phi_0 + U$	$\frac{2}{b\phi_0 R^3} \tilde{G}\left(\frac{z}{R}\right)$
$\xi \ll z \ll R$	LH	$\phi_0 \left(1 - \frac{4}{\sqrt{\pi}} \frac{z}{R}\right)$	$\frac{4}{\sqrt{\pi}} \phi_0 \frac{z}{R}$	$\frac{\phi_0 z^2}{2R^2}$	$\frac{2}{b\phi_0 R^3} \left(-0.308 + \frac{z}{4R}\right)$
$b \ll z \ll \xi$	LH	$\frac{2}{z^2}$	$\frac{4}{3\sqrt{\pi}} \phi_0 \frac{z}{R}$	$\frac{1}{72} \phi_0 \frac{z^4}{R^2 \xi^2}$	$\frac{2}{z^2}$

The molecular field in the asymptotic limit is

$$U^{(0)}(z) = \phi^{(0)}(z) - \phi_0 = \frac{\phi_0}{\sinh^2\left(\frac{z}{2\xi} + \beta\right)} \quad (94)$$

The contributions of loops and tails in the region  $z \gg \xi$ , in the asymptotic limit, can be directly obtained from the partition function of an ideal chain submitted to an external field  $U_0(z)$  and interacting with the wall. The potential  $U_0(z)$  is local with a characteristic scale of order  $\xi$ , its effect in the region  $z \gg \xi$  can therefore be accounted for by a boundary condition at  $z = 0$ . The proper effective boundary condition (which is the only one compatible with the ground state solution  $\psi = \text{const}$  for  $z \gg \xi$ ) is  $\psi'(0) = 0$ . This condition means that the wall and the potential can be replaced by an effective mirror located at  $z = 0$ . Using the image charge principle, we get the partition functions of  $Z_a$  and  $Z_f$  corresponding to the adsorbed and free states:

$$Z_l(n, z) = 2 \int_0^z \frac{dz}{\sqrt{4\pi n}} \exp\left(\frac{z^2}{4n}\right); \quad Z_a(n, z) = 1 - Z_f(n, z) \quad (95)$$

Substituting eqs 95 into eqs 72a–27c we find

$$\phi_l(z) = \phi_0 P_l(z/R); \quad P_l(x) = 4i^2 \text{erfc}(x) \quad (96a)$$

$$\phi_t(z) = \phi_0 P_t(z/R); \quad P_t(x) = 8i^2 \text{erfc}(x/2) - 8i^2 \text{erfc}(x) \quad (96b)$$

$$\phi_f(z) = \phi_0 P_f(z/R); \quad P_f(x) = 1 - P_a(x) \quad (96c)$$

where  $P_a(x) = P_l(x) + P_t(x)$ .

Taking into account the fact that loops dominate in the crossover region  $z \sim \xi$ , we combine eqs 92 and 96a and obtain the loop concentration as

$$\phi_l(z) = \phi_0 \coth^2\left(\frac{z}{2\xi} + \beta\right) P_l\left(\frac{z}{R}\right) \quad (97)$$

However the same matching is not possible for the tail and the free chain concentrations,  $\phi_t$  and  $\phi_f$  since these contributions are subdominant in the region  $z \sim \xi$ . The variations of  $\phi_t(z)$  and  $\phi_f(z)$  in the crossover region can, however, be derived from eqs 30, 35, and 42–44. Even though the formalism described in section 3 is not valid everywhere in the concentrated regime, these equations remain valid in the region  $z \ll R$ . The relationship (89) between the function  $\psi(z)$  and the order parameters  $\varphi(z)$ ,  $\varphi_f(z)$ , and  $\psi_f(z)$ , also remains valid, and these three parameters are given in the region  $z \ll R$  by the right hand side of eq 89 with different prefactors. Matching

the results with the behavior at large distances  $z \ll R$ , we obtain the crossover results

$$\phi_t(z) = \phi_0 f_t\left(\frac{z}{2\xi}, \beta\right) P_t\left(\frac{z}{R}\right) \quad (98)$$

$$\phi_f(z) = \phi_0 f_f\left(\frac{z}{2\xi}, \beta\right) P_f\left(\frac{z}{R}\right) \quad (99)$$

where

$$f_t(x, \beta) = \coth(x + \beta) \frac{f(x + \beta) - f(\beta)}{1 - f(\beta)}$$

$$f_f(x, \beta) = \left[ \frac{f(x + \beta) - f(\beta)}{1 - f(\beta)} \right]^2; \quad f(x) = \coth(x) - 1/x \quad (100)$$

The loop, tail, and free chain contributions to the monomer density in the asymptotic approximation are given by eqs 97–100, which are valid at all distances  $z$ . The asymptotic behaviors of the various concentrations are collected in Table 5. The total monomer concentration rapidly tends to  $\phi_0$  in the region  $z \gg \xi$ : the difference  $\phi - \phi_0$  decays exponentially in this region. In the next section, we discuss finite size corrections to these asymptotic results.

**B. Finite Size Corrections.** The total monomer concentration in the region  $z \gg \xi$  has two finite size corrections to the asymptotic value  $\phi(z) = \phi_0$ . One is due to the approximate solution calculated for the ideal chains in a *given* external potential  $U_0$ , and the other one is due to the correction to the potential  $U_0$  itself. We first discuss the first correction,  $\delta\phi_1(z)$ . Since there is only one characteristic length scale (namely  $R$ ) in the region of interest, the correction is a universal function of  $z/R$  with a nonuniversal prefactor:

$$\delta\phi_1(z) = A F_1(z/R) \quad (101)$$

The end point density can also be written in the same dimensionless form:

$$\delta\rho_1(z) = \frac{A}{N} G_1(z/R) \quad (102)$$

The nonuniversal prefactor  $A$  is found using the following trick.

The asymptotic behavior for the concentration intrinsically implies a correction. The total excess amount of monomers near the wall in the asymptotic limit is

$$\Gamma_\phi^{(0)} = \int [\phi^{(0)}(z) - \phi_0] dz = \phi_0 \int [\psi^2(z) - 1] dz \quad (103)$$

where  $\psi(z)$  is defined in eq 8. The *same* quantity can also be calculated by counting the excess number of

chain end points  $\Lambda_6 = \int [\rho(z)/v] - [2\phi_0/Nv] dz$ . The total excess of monomers is then  $\Gamma_\rho = (Nv/2)\Lambda_6$  since two excess ends correspond to an excess volume  $Nv$ . We therefore obtain

$$\Gamma_\rho^{(0)} = \phi_0 \int [\psi(z) - 1] dz \quad (104)$$

The two expressions for the same quantity are thus different:  $\Gamma_\phi^{(0)} \neq \Gamma_\rho^{(0)}$ . The difference  $\Delta^{(0)} \equiv \Gamma_\phi^{(0)} - \Gamma_\rho^{(0)}$  must be compensated by the corrections:  $\Delta^{(0)} = \delta\Gamma_\rho - \delta\Gamma_\phi$ , where  $\delta\Gamma_\phi = \int \delta\phi_1(z) dz$ ,  $\delta\Gamma_\rho = \int \delta\rho_1(z) dz$ . The prefactor  $A$  is thus equal to

$$A = C\delta^{(0)}/R = C\frac{\phi_0}{R} \int [\psi^2 - \psi] dz \quad (105)$$

where  $C$  is an unknown universal numerical constant that can be expressed as a function of the integrals of the dimensionless functions  $F_1(z/R)$  and  $G_1(z/R)$ . Using eq 8 we estimate  $A \sim 1/bR$  so that  $A \ll \phi_0$  in the region  $\phi \gg \phi_2$ , as expected.

The other correction,  $\delta\phi_2$ , is due to the large scale correction to the molecular field,  $\delta U(z) = \delta\phi(z)$ :

$$\delta\phi_2 = -\hat{\kappa}_0 \delta U$$

where  $\hat{\kappa}$  is the generalized susceptibility of the system, which is in fact an integral operator. For a smooth potential  $\delta U$  with a characteristic scale of order  $R$  (or larger) we use the zero wavevector susceptibility of a Gaussian chain  $\hat{\kappa}_0 \sim N\phi_0$ . [The last equation can be easily verified in the limit of very smooth  $\delta U$  with characteristic wavelength  $\gg R$ . Note that  $N\delta U$  is the chain potential energy; thus the distribution of chain ends is  $\rho(z) = \text{const} \exp[-N\delta U(z)]$ , so that  $\delta\phi/\phi_0 = -N\delta U$ .] Thus we write

$$\delta\phi = \delta\phi_1 + \delta\phi_2 = \delta\phi_1 - \hat{\kappa}_0(\delta\phi)$$

or  $(1 + \hat{\kappa}_0)\delta\phi = \delta\phi_1$ . Taking into account that for concentrated solutions,  $N\phi_0 \gg 1$ , we get

$$\delta\phi(z) \simeq \hat{\kappa}_0^{-1} \delta\phi_1 = \frac{A}{N\phi_0} F(z/R) \quad (106)$$

where  $F$  is a universal function. The total correction to the concentration profile can then be expressed as

$$\delta\phi(z) = \frac{1}{N^{3/2}} \left\{ \int_0^\infty [\psi^2 - \psi] dz \right\} F\left(\frac{z}{R}\right) \quad (107)$$

The numerical constant  $C$  has here been absorbed in the definition of  $F$ . Equation 107 can also be derived in a more rigorous way from the general form (18) of the solution of the basic eq (17).

The universal function  $F$  can be calculated directly from linear response theory by considering a very concentrated solution or a very weakly adsorbing wall:  $b \gg \xi$ . In this case,  $\phi(z) - \phi_0$  is small everywhere compared to  $\phi_0$  and the adsorbing wall can be considered as a perturbation. The boundary condition (7) is equivalent to an attractive potential  $-(1/b)\delta(z - 0)$ . Using also the image charge principle, we replace the wall by a double well (two  $\delta$ -wells to the right and to the left of the plane  $z = 0$ , separated by an infinitesimal distance); thus the equivalent external potential is

$$U_s(z) = -\frac{2}{b}\delta(z) \quad (108)$$

The perturbation of the monomer density induced by  $U_s$  is

$$\delta\phi(z) = -\hat{\kappa} U_s(z) = \frac{2}{b}\kappa(z) \quad (109)$$

where  $\hat{\kappa} U_s(z) \equiv \int \kappa(z - z') U_s(z') dz'$ ,  $\kappa(z) \equiv \int \kappa_q e^{iqz} (dq/2\pi)$ . Here  $\kappa_q$  is the generalized susceptibility of the system, which can be calculated using the random phase approximation (RPA). The result is well-known:<sup>13</sup>

$$\kappa_q = \frac{\kappa_0(q)}{1 + \kappa_0(q)}; \quad \kappa_0(q) = \phi_0 N g_D(Nq^2) \quad (110)$$

where  $\kappa_0(q)$  is the susceptibility of the corresponding ideal system of noninteracting chains and  $g_D$  is the Debye function,

$$g_D(x) = \frac{2(x - 1 + \exp(-x))}{x^2}$$

In the limit where  $\phi_0 N \gg 1$ , we represent  $\kappa_q$  as

$$\kappa_q \simeq \frac{\phi_0 N}{(\phi_0 N + 0.5) + 0.5 N q^2} + \frac{G(Nq^2)}{\phi_0 N}; \quad G(x) \equiv \frac{x + 1}{2} - \frac{1}{g_D(x)} \quad (111)$$

where terms of order  $(1/\phi_0 N)^2$  and higher order terms are omitted; the function  $G$  has been defined in such a way that it vanishes when  $x$  is large. After Fourier transformation of eq 111, we get

$$\kappa(z) \simeq \frac{1}{2\xi} \exp\left[-\left(\frac{z}{\xi}\right)\right] + \frac{1}{\phi_0 N^{3/2}} \tilde{G}\left(\frac{z}{R}\right) \quad (112)$$

where

$$\tilde{G}(x) = \int G(k^2) \exp(ikx) \frac{dk}{2\pi} \quad (113)$$

and we neglected a slight renormalization of the correlation length,  $\xi$ .

The second long-scale term in the right hand side of eq 112 gives the finite size correction to the concentration (the first short-scale term is exponentially small in the region  $z \gg \xi$ ). Using eqs 109 and 112, we finally obtain the large-scale perturbation of the monomer density which is valid if  $b \gg \xi$ :

$$\delta\phi(z) \simeq \frac{2}{b\phi_0 N^{3/2}} \tilde{G}\left(\frac{z}{R}\right) \quad (114)$$

Comparing now eqs 107 and 114, we obtain

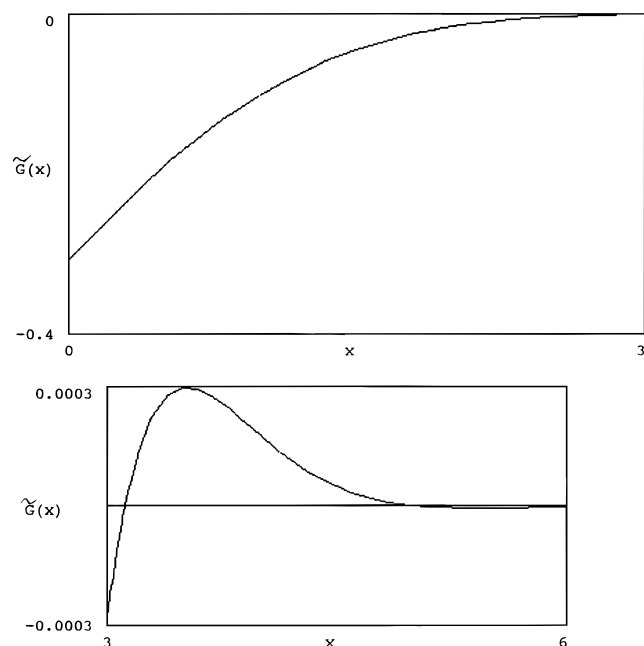
$$F\left(\frac{z}{R}\right) = 4\tilde{G}\left(\frac{z}{R}\right) \quad (115)$$

This gives the correction to the concentration profile in the general case:

$$\delta\phi(z) = \frac{8\xi}{N^{3/2}} \tilde{A}\left(\frac{\xi}{b}\right) \tilde{G}\left(\frac{z}{R}\right) \quad (116)$$

where

$$\tilde{A}(x) = \ln 2 - 1 + x + \sqrt{x^2 + 1} - \ln(x + 1 + \sqrt{x^2 + 1})$$



**Figure 3.** Reduced correction to the bulk concentration ( $\phi_0$ ) in the concentrated regime for  $z > \xi$ :  $\tilde{G}(z/R)$  vs  $z/R$ .

In particular in the region  $\phi_2 \ll \phi_0 \ll 1/b^2$  the total concentration profile  $\phi(z) = \phi^{(0)}(z) + \delta\phi(z)$  is

$$\phi(z) \simeq \phi_0 \coth^2\left(\frac{z}{2\xi} + \beta\right) + \frac{8}{b\phi_0 N^{3/2}} \tilde{G}\left(\frac{z}{R}\right) \quad (117)$$

The magnitude of the perturbation in the crossover region  $\phi_0 \sim \phi_2$  is thus  $\delta\phi \sim 1/N$ . Note that this result is consistent with eq 83; our results for the concentrated and semidilute regimes cross over smoothly at  $\phi_0 \sim \phi_2$ .

The universal function  $\tilde{G}(x)$  is plotted in Figure 3; it reaches a minimum at  $x = 0$ , and a weak maximum at  $x \simeq 3.5$  where  $\tilde{G}(3.5) \simeq 3 \times 10^{-4}$ . The function is characterized by the following asymptotic behaviors

$$\tilde{G}(x) = \begin{cases} -0.308 + 0.25x, & x \ll 1 \\ 1.39 \sin(1.68x + 0.922) \exp(-2.218x), & x \gg 1 \end{cases} \quad (118)$$

The monomer density  $\phi(z)$  shows thus damped oscillations in the region  $z > R$ ; note, however, that the amplitude of these oscillations is always very small. Another interesting conclusion which can be drawn from eq 117 is that the variation of  $\phi(z)$  is nonmonotonic even in the region  $z \ll R$ ; the monomer density reaches the first minimum in the "correlation" region near the wall, at  $z = z_{\min} = \xi \ln(bR^4/4\xi^5)$ , so that  $\phi(z)$  is increasing slowly in the region  $z_{\min} < z < 3.5R$ . This feature disappears in the crossover region,  $\phi_0 \sim \phi_2$ ; for  $\phi_0 < \phi_2$  the monomer density is decreasing in the whole region between the wall and the cutoff length (see Table 4).

Finally, the value of the bound state energy  $\epsilon$  in the concentrated region can be calculated by generalizing the perturbation scheme. This leads to

$$\epsilon = \left(\frac{4}{b\phi_0 N}\right)^2, \quad \phi_2 \ll \phi_0 \ll 1/b^2 \quad (119)$$

The binding energy  $\epsilon N \sim (\phi_2/\phi_0)^2$  is small in the whole concentrated regime, as expected.

As a summary of this section, we present in Figure 4 qualitative sketches of the concentration profiles in the various regimes that show the different relevant length scales.

## VII. Scaling Theory

In this section, we use scaling arguments to generalize the results obtained in the mean field approximation to polymers in a good solvent where the excluded volume correlations play an essential role at short distances. The concentration profile of a semidilute polymer solution close to an adsorbing surface has been constructed by de Gennes.<sup>5</sup> Locally, the solution has the same structure as a bulk semidilute solution but with a mesh size decreasing toward the adsorbing surface. The scaling ansatz that leads to a de Gennes self-similar profile is that the local correlation length is proportional to the distance  $z$  from the wall. This leads to a concentration profile decaying as

$$\phi(z) \simeq z^{1/\nu-d} \quad (120)$$

where  $\nu$  is the swelling exponent of a polymer chain in a good solvent (approximately equal to  $3/5$ ) and  $d$  is the space dimension that we keep here as a variable, the useful case corresponding to  $d = 3$ . This self-similar profile is cut off at large distances at the bulk correlation length  $\xi$  in a semidilute solution or at the chain radius of gyration  $R \simeq N^\nu$  in a dilute solution; beyond the bulk correlation length, the concentration has the bulk value  $\phi_0$ . At small distances, the self-similar profile is cut off at the distance  $b$  which characterizes the wall attraction. In order to ignore the complicated proximal effects, we consider here only the strong adsorption limit where  $b \sim a$ .<sup>24</sup>

We now discuss the relative importance of loops and tails in the adsorbed layer over the whole concentration range from dilute to concentrated solutions using scaling arguments based on those of Semenov and Joanny<sup>12</sup> for adsorption from dilute solutions. We also assume throughout that the qualitative picture of the structure of the adsorbed layer that emerges from the mean field theory remains valid.

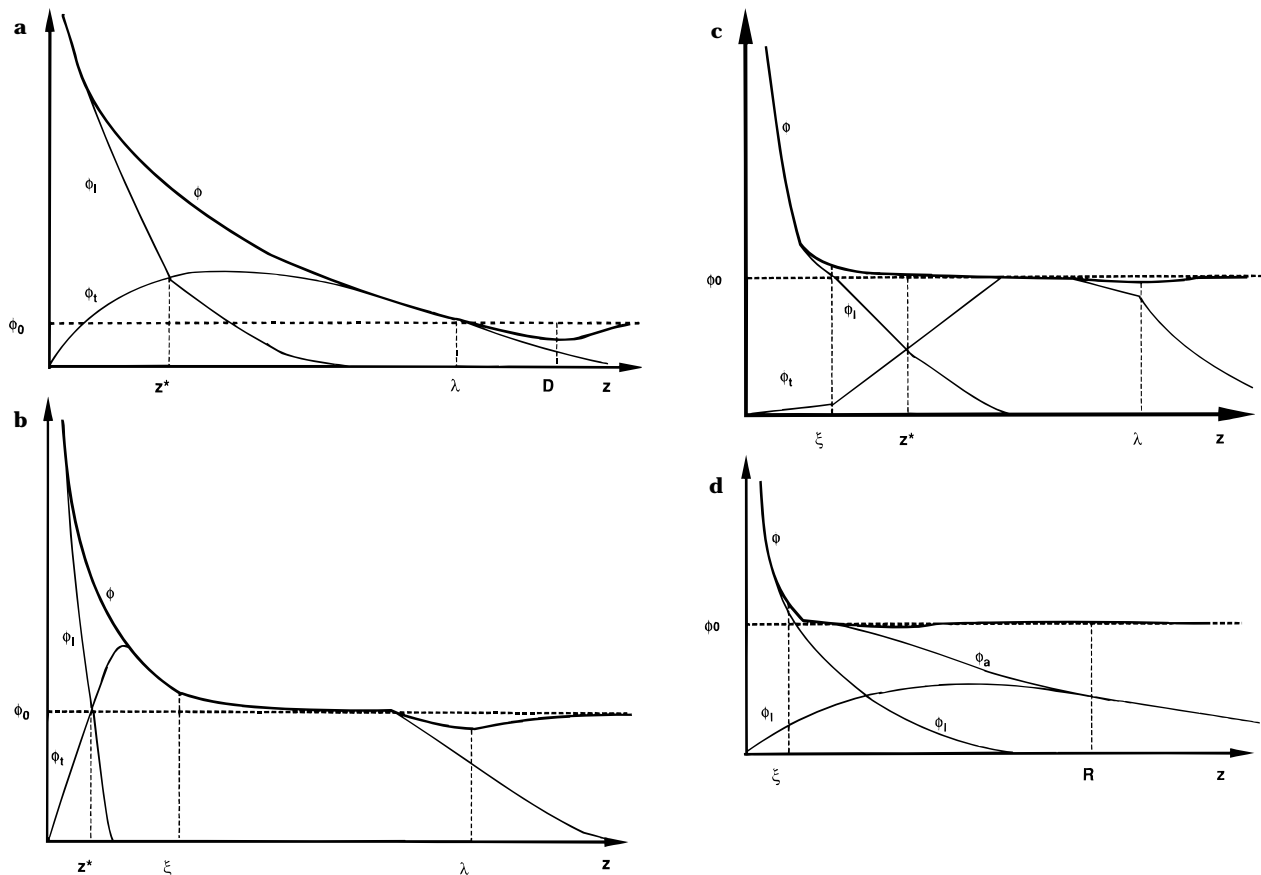
**A. Scaling Approach in a Dilute Solution.** The structure of a polymer layer adsorbed from a dilute solution has been discussed in ref 12, we summarize here the arguments. The self-similar structure of the adsorbed layer imposes that the surface density of chain sections (loops or tails) of size larger than  $n$  is of order one per local mesh of area  $\xi(z)^{d-1}$ , where  $\xi(z)$  is the local correlation length  $\xi \simeq z \simeq n^\nu$ . Close to the wall, loops dominate over tails and the distribution of loop sizes is  $Z_l(n) \simeq n^{-\nu(d-1)-1}$ . This distribution  $Z_l(n)$  is also, in the language used above, the partition function of a loop of size  $n$ . The partition function of a tail of  $n$  monomers can be calculated from that of a loop of  $2n$  monomers by joining the free end points of two tails to form a loop. The partition function of a loop is thus related to that of a tail by

$$Z_l(n) \approx Z_t^2(n/2) n^{-\nu} n^{1-\gamma} \quad (121)$$

where  $\gamma \simeq 1.16$  is the susceptibility exponent. Therefore from the partition function of a tail is

$$Z_t(n) \simeq n^{(-\nu(d-2)+\gamma)/2-1} \quad (122)$$

The concentration of chain end points can be directly



**Figure 4.** Qualitative sketch of the concentration profiles showing the relevant length scales: (a) dilute regime; (b) semidilute tail regime; (c) semidilute loop regime; (d) concentrated regime.

calculated from the tail partition function, the normalization is given by the total number of end points  $2\Gamma/N$  where  $\Gamma \approx a^{-(d-1)}$  is the adsorbance. We obtain  $\rho_a(z) \propto z^{-\beta/\nu}$  where the exponent  $\beta$  is equal to  $(\nu d - \gamma)/2$ ,  $\beta/\nu \sim 1/2$ . In the magnetic analog to the polymer problem, the concentration of end points corresponds to the order parameter which decays with the exponent  $\beta/\nu$ . From the chain end concentration, we determine the concentration of monomers belonging to tails

$$\phi_t(z) \approx \int_z^R dz' \rho_a(z') \frac{dn}{dz} \approx \frac{1}{N} z^{(1/\nu)-1} \quad (123)$$

where  $n = n(z) \sim z^{1/\nu}$  is the typical number of links in a blob of size  $z$  (note that  $a$  is the unit length).

The concentration of monomers belonging to tails grows from the wall and becomes larger than the concentration of monomers belonging to loops at  $z^*$

$$z^* \approx N^{1/(d-1)} \quad (124)$$

Further away from the wall ( $z > z^*$ ), the concentration is no longer dominated by loops but by the tail contribution. The mean field theory suggests that the concentration still decays as the same power law  $z^{1/\nu-d}$ , as in the loop region with a different (higher) prefactor. The tail partition function can then be calculated from the concentration profile and the loop partition function from eq 121:

$$Z_t \approx N^{(\gamma+\nu d)/2\nu(d-1)} n^{-1-\nu(d-1)} \quad (125)$$

$$Z_l \approx N^{(\gamma+\nu d)/\nu(d-1)} n^{-1-\gamma-\nu(2d-1)} \quad (126)$$

Using eqs 122 and 125 we get the end concentration:

$$\rho_a(z) \approx \frac{1}{N z^*} \left( \frac{z}{z^*} \right)^{-\beta/\nu} \quad z < z^*; \quad \rho_a(z) \approx \frac{1}{z^d} \quad R > z > z^* \quad (127)$$

The concentration of monomers belonging to loops decays then (in the region  $R > z > z^*$ ) with a high power of  $z$

$$\phi_l(z) \approx N^{(\gamma+\nu d)/\nu(d-1)} z^{(-2\nu d+1-\gamma)/\nu} \quad (128)$$

As suggested by the mean field theory, there is only one characteristic length scale  $z^*$  in the central region  $b < z < R$ , and all the concentration profiles can be written in a scaling form  $\phi_{l,t} \approx z^{1/\nu-d} f(z/z^*)$ . The scaling function  $f$  for the total concentration reaches a finite value at both large and small values of  $z$ . The distal region ( $z > R$ ) is thus almost only built up by tails; the tail concentration in this region decays exponentially over the radius  $R$  (we do not consider here the logarithmic dependence of the cutoff length on the bulk concentration).

**B. Scaling Theory in a Semidilute Solution.** We now discuss the relative importance of loops and tails in a semidilute solution. As in the mean field theory, two characteristic concentrations play an important role.<sup>25</sup> The concentration  $\phi_l$  is reached when the bulk correlation length is equal to the crossover distance  $z^*$

$$\phi_l \approx N^{(1-\nu d)/\nu(d-1)} \approx N^{-2/3} \quad (129)$$

The concentration  $\phi_2$  is reached when the adsorbance due to the large loops or tails  $\phi R(\phi)$  (where  $R(\phi) \approx N^{1/2} \phi^{(2\nu-1)/2(1-\nu d)}$  is the radius of a chain in a semidilute solution) is of the order of the contribution of the small loops (the surface excess  $\Gamma \approx a^{1-d}$ ).

$$\phi_2 \approx N^{(1-\nu d)/(2\nu(d-1)-1)} \approx N^{-4/7} \quad (130)$$

When the bulk concentration  $\phi_0$  is larger than  $\phi_2$ , in a concentrated solution, the semidilute solution can be considered as a melt of blobs. At distances smaller than  $\xi$ , in the adsorbed layer, the concentration decays as  $z^{1/\nu-d}$  and the concentration of loops is the same as in a dilute solution in the loop region close to the wall. At distances larger than  $\xi$ , the mean field results of section 6 can be used with a correlation length  $\xi$  and a radius  $R$  given by their values in a semidilute solution in a good solvent.

**1. Semidilute-Tails Regime ( $\phi^* < \phi_0 < \phi_1$ ).** In this regime the crossover size  $z^*$ , where the tails become more important than the loops, is smaller than the bulk correlation length  $\xi$ . Most of the end points are thus located inside the adsorbed layer of thickness  $\xi$  and therefore most of the chains are trapped inside the adsorbed layer. The crossover distance has the same variation with molecular weight as in a dilute solution. Similarly, eqs 123, 126, and 128 hold for the partition functions and the concentration profiles inside the adsorbed layer ( $z < \xi$ ). The large tails and a few loops are dangling in the solution outside the adsorbed layer. The large tails build up a finite fraction of the concentration between  $\xi$  and the chain radius  $R$  and have Gaussian statistics at this length scale. The partition function of large tails scales then as  $Z_t \approx n^{-3/2}$ . Matching the tail partition functions inside and outside the layer leads to the explicit scaling form:

$$Z_1(n) \approx N^{(\gamma+\nu d)/2\nu(d-1)} g^{-1-\nu(d-1)} \left(\frac{n}{g}\right)^{-3/2} \quad (131)$$

where  $g \approx \xi^{1/\nu}$  is the number of monomers per blob in the bulk. The partition function of a large loop  $Z_l$  can be related to that of a large tail  $Z_t$  using the same trick as in a dilute solution

$$Z_1(n) \approx Z_t^2(n/2) \left(\frac{n}{g}\right)^{-1/2} g^{1-\gamma-\nu} \quad (132)$$

If we consider the chain as a chain of blobs, the connection of the two tails to form a loop requires the connection of the last blob of each tail which gives the first two factors in the right hand side of eq 132 and inside this last blob the meeting of the two end points which gives the last factor. The partition function of a large loop then reads

$$Z_l(n) \approx N^{(\gamma+\nu d)/\nu(d-1)} g^{\nu-1-2\nu d-\gamma} (n/g)^{-7/2} \quad (133)$$

From the partition functions we calculate the chain end concentration  $\rho_a$  and the concentration of monomers belonging to large loops  $\phi_l$ .

$$\rho_a(z) = \frac{1}{\xi^d} \left(\frac{z}{\xi}\right)^{-2} \quad (134a)$$

$$\phi_l(z) = \phi_l(\xi) \left(\frac{z}{\xi}\right)^{-4} \quad (134b)$$

Only a fraction  $(z^*/\xi)^{d-1}$  of the end points belonging to

adsorbed chains is found outside the adsorbed layer. A finite fraction of the chain ends is located on either side of  $z^*$  inside the adsorbed layer. At the concentration  $\phi_1$ ,  $z^*$  becomes equal to the bulk correlation length and a finite fraction of ends belonging to adsorbed chains is located in the bulk of the solution. One can also check that these scaling results are in agreement with the mean field results of Table 3 in the limit  $d = 4$ ,  $\nu = 1/2$ .

**2. Semidilute-Loops Regime ( $\phi_1 < \phi_0 < \phi_2$ ).** In this regime the adsorbed chains form large loops outside the adsorbed layer. The crossover between loop and tail dominance is located in the bulk solution,  $z^* > \xi$ . Large loops dominate over tails just outside the adsorbed layer, and build up there a finite fraction of the bulk concentration. The large loop partition function is obtained by matching at  $z \approx \xi$  the loop partition function,  $Z_l(n) \propto n^{-3/2}$ , outside the adsorbed layer to the loop partition function in the adsorbed layer (which is identical to that of the dilute case when  $z \ll z^*$ ):

$$Z_l \approx Z_l(g) \left(\frac{n}{g}\right)^{-3/2} \quad (135)$$

Wherefrom we obtain the large tail partition function:

$$Z_t \approx Z_t(g) \left(\frac{n}{g}\right)^{-1/2} \quad (136)$$

The partition functions show that most ends of the adsorbed chains are located behind the adsorption layer. Close enough to the adsorption layer, in the region  $\xi < z < z^*$ , the concentration built up by the large tails reads

$$\phi_t \approx \frac{Z}{N} g^{1-2\nu} \quad (137)$$

The concentration due to the tails increases from the wall and reaches the concentration due to the large loop at  $z = z^*$ :

$$z^* \approx N g^{-(d-2)\nu} \approx N \phi_0^{(d-2)\nu/(d\nu-1)} \quad (138)$$

Further away from the wall, the large tails dominate and build up a finite fraction of the bulk concentration. The partition function of the large tails beyond  $z^*$  ( $n > n^* \approx z^{*1/\nu}$ ) is

$$Z_t \approx Z_t(g) \left(\frac{n^*}{g}\right)^{-1/2} \left(\frac{n}{n^*}\right)^{-3/2} \quad (139)$$

and the related partition function of large loops ( $n > n^*$ ):

$$Z_l \approx Z_l(g) \left(\frac{n^*}{g}\right)^{-3/2} \left(\frac{n}{n^*}\right)^{-7/2} \quad (140)$$

The concentration due to the large loops has a fast power law decay beyond  $z^*$

$$\phi_l(z) \approx \phi_l \left(\frac{z}{z^*}\right)^{-4} \quad (141)$$

Only a fraction  $\xi/z^*$  of the ends belonging to adsorbed chains are located within the adsorbed layer in this regime. A finite fraction of the ends is found on either side of  $z^*$  beyond the adsorption layer. The end concentration scales as

$$\rho_a(z) \approx \frac{1}{Nz^*} \left( \frac{z}{\xi} \right)^{-\beta/\nu} \quad z < \xi \quad (142a)$$

$$\rho_a(z) \approx \frac{1}{Nz^*} \quad \xi < z < z^* \quad (142b)$$

$$\rho_a(z) \approx \frac{1}{Nz^*} \left( \frac{z}{z^*} \right)^{-2} \quad z^* < z \quad (142c)$$

At the concentration  $\phi_2$  where the adsorbance becomes dominated by large loops and tails, the crossover length  $z^*$  becomes equal to the semidilute chain radius; in the concentrated regime,  $z^*$  becomes a fraction of the chain radius and is not a specific scale.

### VIII. Concluding Remarks

In this paper, we have considered the equilibrium adsorption of linear polymers using a mean field approach. We have studied both cases of strong ( $\epsilon N \gg 1$ ) and weak ( $\epsilon N \ll 1$ ) adsorption, where  $\epsilon N$  is the effective adsorption or binding energy per chain. Most of the results correspond to the strong adsorption limit (sections 4 and 5) which is the most relevant from the experimental point of view. The results have also been extended to good solvents using a scaling analysis.

One of the main messages is that the ground state dominance approximation ( $\epsilon N \gg 1$ ) is not sufficient to ensure the validity of the classical approach outlined in section 2. Most of the qualitatively new features are connected with the existence of chain tails: we find a wide region away from the wall ( $z^* < z < \lambda$ ) where the contribution of tails to the monomer concentration is dominant. The formalism developed in section 3 allows a quantitative analysis over the whole concentration range of the different contributions to the monomer concentration (due to loops, tails, and free chains) in terms of four basic functions  $\psi$ ,  $\varphi$ ,  $\psi_f$ , and  $\varphi_f$  in the general case and two ( $\psi$ ,  $\varphi$ ) in the absence of free chains. [Note that in most cases the last function,  $\varphi_f$ , can be related to  $\varphi$  by eq 68, so only three functions are independent.] All the concentration profiles are related to these functions which can be found as a solution of a system of differential equations (35), (29), (43), and (44).

The tails are expelled from the region close to the adsorbing wall and thus induce a thickening of the adsorbed layer, i.e. an increase of concentration away from the wall in the region  $z \gtrsim z^*$ . This effect increases with the number of tails which in turn is inverse proportional to the polymer molecular weight. We therefore predict an anomalous variation of the monomer adsorbance  $\Gamma$  which decreases with molecular weight in the asymptotic limit of very large molecular weights.

The thickening effect of chain tails also makes the adsorption layer less penetrable to free chains. For example at a bulk concentration  $\phi_0 = \phi_1 = 1/(bN)^{2/3}$  the tail effect induces a reduction of the penetration factor of free chains  $p_f$  by a large number  $\sim N/b^2$ .

Another interesting qualitative feature is the depletion hole in the concentration profile that exists at any bulk concentration at a distance  $z_{\min}$  from the wall where the concentration reaches a minimum value  $\phi < \phi_0$ . In most regimes the distance  $z_{\min}$  is of the order of the cutoff distance  $\lambda$ , which is comparable to the radius of gyration  $R$ . However it can be much larger than  $R$  for a very dilute bulk solution,  $\phi_0 \ll 1/N$ , or much smaller than  $R$  in the concentrated regime,  $\phi_0 \gtrsim \phi_2$ .

In the whole paper we have assumed that the attraction to the wall is strong enough that the extrapolation length,  $b$ , is much shorter than  $R = \sqrt{N}$ . The case  $b \gg$

$R$  is simpler: in this regime an RPA perturbation approach similar to that done in section 6.2 is applicable at all concentrations. Using this approach one finds a monomer concentration profile with multiple minima which is characteristic for a concentrated regime ( $\phi > 1/N$ ), that smoothly crosses over to a density profile with essentially a single minimum in the region  $\phi \ll 1/N$ .

The mean field theory presented in this work corresponds to the asymptotic limit of large molecular weights of the general mean field theory. The general mean field theory of polymer adsorption has been studied extensively numerically by the Wageningen group.<sup>1</sup> The double layer structure of a polymer layer adsorbed from a dilute solution with an inner layer dominated by loops and an outer layer dominated by tails has been discussed long ago by this group. The concentration of monomers belonging to tails shows a maximum in the vicinity of the crossing point between the concentrations of monomers belonging to loops and tails. Recent results show a good agreement with eq 53 for the position of this maximum.<sup>26</sup> In the region dominated by loops, a power law decay of the concentration as  $1/z^2$  is observed. In the tail region no power law is observed. This is probably due to the fact that the crossover to the asymptotic behavior is rather broad in this region, as shown in Figure 1, and that with the molecular weight values which are accessible (and which correspond reasonably well to the experiments) the cutoff length  $\lambda$  is not well separated from the crossover length  $z^*$ . In the cutoff region, the concentrations of tails and loops decay both exponentially and the decay length of the tail concentration is twice that of the loop concentration. Numerically, the adsorbance always increases with molecular weight,<sup>1</sup> as discussed in section 4.1 the true asymptotic behavior where the adsorbance decreases with the concentration would require extremely high molecular weights. A detailed comparison between our mean field theory and the numerical self-consistent field calculations is presented elsewhere.<sup>27</sup>

**Acknowledgment.** We thank K. Van der Linden for discussions on her numerical results and J. Baschnagel for a critical reading of the manuscript. This work was performed during the stay of one of the authors (A.N.S.) at Université Louis Pasteur in Strasbourg (Institut Charles Sadron). A.N.S. would like to thank the University and the Ministry of Higher Education of France for the opportunity to stay in Strasbourg.

### Glossary

$a$	statistical segment size divided by $\sqrt{6}$
$b$	extrapolation length
$B$	proportionality constant $\rho_a = B\psi$ , $\phi_t = B\psi\phi$
$c(\mathbf{r})$	monomer concentration profile
$c_0$	bulk concentration
$c_e$	end concentration
$d$	dimension of space
$D$	range of the attraction felt by a chain facing the adsorption layer
$E_0$	bound state eigenvalue
$E_s$	eigenvalue of the Edwards equation for $Z(n, z)$
$\bar{F}$	grand canonical potential
$F_1(z)$	free energy of a chain with its end at $z \gg R$
$F_{\text{conf}}$	configurational free energy
$F_{\text{int}}$	interaction free energy between monomers
$F_s$	surface free energy

$g$	Pincus blob of a stretched chain, blob size in the bulk solution
$g_D(x)$	Debye function
$K$	integral of the order parameter $\psi(z)$
$K(q)$	integral of $\psi(q, z)$
$K_s$	amplitude of $\psi_s$ in the eigenmode expansion of $Z(n, z)$
$i^{\nu}\text{erfc}(x)$	repeated integral of the complementary error function
$l$	natural unit length in the central region (dilute regime)
$\tilde{n}$	number of monomers of a Gaussian subchain crossing the free chain depletion layer $\tilde{n} \approx \lambda_f^2$
$n^*$	chain size associated with $z^*$ , $n^* \approx z^{*1/\nu}$
$n_c$	cutoff tail size
$N$	number of monomers per chain
$N_c$	chain length for which $\Gamma$ is maximum
$p_f$	permeability of the layer to free chains $p_f = \phi_f(b)/\phi_0$
$R$	Gaussian radius of gyration
$T$	temperature
$U$	molecular potential
$\tilde{U}$	reduced $U$ in the central region (dilute regime)-
$U_{\text{int}}$	interaction molecular field
$U_s$	surface potential, surface molecular field
$U_{\text{tot}}$	total molecular field
$\nu$	Edwards excluded volume parameter
$z^*$	distance from the wall where the tail monomer and the loop monomer concentrations cross
$z_1$	crossover from hair pin penetration to end penetration
$Z(n, z)$	partition function of a chain of length $n$ with one end at position $z$
$Z_a(N, z)$	adsorbed configuration contribution to $Z(N, z)$
$Z_f(N, z)$	free configuration contribution to $Z(N, z)$
$Z_l(n)$	partition function of a loop of size $n$
$Z_t(n)$	partition function of a tail of size $n$
$Z_{\text{tail}}(n, z)$	partition function of a tail of $n$ monomers ending at $z$
$\gamma$	partition function exponent of polymers in a good solvent
$\Gamma$	adsorbance
$\Gamma_0$	adsorbance for infinite chain length
$\Gamma_1, \Gamma_2$	finite size corrections to $\Gamma$
$\Gamma_l$	contribution of the loops to the adsorbance
$\Gamma_t$	contribution of the tails to the adsorbance
$\delta(z)$	relative depletion hole depth
$\epsilon$	adsorption energy per monomer $\epsilon = -E_0$
$\zeta$	reduced distance $z/l$ in the central region (dilute regime)
$\hat{\kappa}_0$	generalized susceptibility at vanishing wave vector
$\kappa_q$	generalized susceptibility of the bulk solution
$\lambda_f$	thickness of the sublayer where free chains are depleted
$\mu_0$	bulk chemical potential
$\nu$	swelling exponent
$\xi$	bulk correlation length
$\rho(z)$	end distribution $\rho(z) = \nu c_e(z)$
$\rho_a(z)$	density of end points of adsorbed chains
$\phi(z)$	monomer volume fraction profile
$\phi^*$	bulk overlap density
$\phi_0$	monomer bulk volume fraction
$\phi_1$	onset of the semidilute loop regime

$\phi_2$	crossover to the regime where the adsorbance is dominated by large tails and loops
$\phi_f(z)$	free chain monomer distribution
$\phi_l(z)$	loop monomer distribution
$\phi_{\text{min}}$	minimum of the total monomer density (in the depletion hole)
$\phi_t(z)$	tail monomer distribution
$\varphi(z)$	order parameter describing the end section dangling beyond $z$
$\tilde{\varphi}(\zeta)$	reduced $\varphi$ in the central region (dilute regime)
$\varphi_f(z)$	order parameter associated with the short tail of a penetrating chain
$\psi(q, z)$	eigenfunction associated with the eigenvalue $q^2$ of the Edwards equation (continuum)
$\psi(z)$	order parameter
$\tilde{\psi}(\zeta)$	reduced $\psi$ in the central region (dilute regime)
$\psi_f(z)$	eigenfunction $\psi(0, z)$ , order parameter associated with a penetrating free chain ending at $z$
$\psi_s$	eigenfunction of the Edwards equation for $Z(n, z)$

## References and Notes

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