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Adsorption of a bidisperse polymer mixture onto a flat wall

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This paper studies the thermodynamic properties of the competitive adsorption between two polymer species differing only in length onto a flat wall from dilute solution by both mean-field and scaling theories. The employed mean-field approach is based on a recently developed theory for monodisperse solutions, which goes beyond the usual ground-state approximation to account for the contribution of the tails. As in the monodisperse case we also find a crossover length z^* which separates a loop-dominated region adjacent to the wall from a tail-dominated region farther away from the wall. This length scale strongly depends on the length of both chains and is the relevant scaling variable for the loop and tail concentration profiles. The space variation of these profiles and the adsorbances are discussed in detail. We find a strong adsorption preference for the long chains, which is very pronounced in dilute solution. This result parallels those of experiments and, in its mean-field version, can be compared quantitatively with the numerical calculations of the Scheutjens-Fleer theory [G. J. Fleer *et al.*, *Polymers at Interfaces* (Chapman and Hall, London, 1993)]. However, mean-field theory predicts that the adsorbances depend only on the ratio of the two chain lengths, whereas an absolute dependence on chain length is found by scaling theory. Since the scaling theory extends the mean-field treatment to good solvent conditions, this qualitative difference between both theoretical approaches should be observable in experiments. [S1063-651X(97)13402-X]

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I. INTRODUCTION

Many polymerization reactions generate samples with a rather large molecular weight distribution. If this polydisperse mixture is exposed to an attractive wall the equilibrium adsorption involves several stages, depending on the overall concentration of the sample [1]. At very low concentrations all polymer chains, irrespective of their length, are adsorbed, and the adsorption isotherm, i.e., the excess amount of polymer per unit area in the interfacial region as a function of concentration, rises steeply. As the concentration increases and the wall becomes more and more covered, the long chains begin to replace the shorter ones. During this process the adsorption isotherm (usually) gradually increases before crossing over to a plateau when the wall is saturated by the large polymers [1–3]. The adsorption preference of the large chains (in dilute and moderately concentrated solutions) is often rationalized as follows [1,5]: When a polymer adsorbs at a wall it loses translational entropy in comparison to the bulk. Since the entropy per chain in the bulk is given by $S \propto (\phi^0/N)\ln(\phi^0/eN)$, where ϕ^0 is the monomer bulk volume fraction and N the chain length, large chains lose less entropy than smaller chains and are thus adsorbed preferentially. Strictly speaking, this argument is not completely correct because the loss in translational entropy is not the only driving force which determines the equilibrium structure of the adsorbed layer. The equilibrium structure results from the balance of the chemical potentials between the free chains in the bulk and the adsorbed chains. The chemical potentials of the adsorbed short and long chains are different due to chain-end effects. How these chain-end effects influence the thermodynamic properties of the layer is one aspect which we want to discuss in this paper. Despite this proviso with respect to the simple entropy argument it suggests that the adsorption preference is more pronounced in dilute solution. This expectation is indeed borne out in experiments and can also be understood theoretically by self-consistent mean-field calculations [1,4–6].

The self-consistent mean-field theory, as developed by Scheutjens, Fleer, and co-workers [1,5–7] analyzes the structural properties of an adsorbed polymer layer in terms of an effective single-chain problem. Each monomer of a chain thereby experiences an average potential consisting of the wall attraction and of the mean-field excluded-volume interaction. Since the excluded-volume interaction again depends on the structure of the layer (i.e., on the average monomer concentration [8]), the theory is self-consistent. From the numerical solution of the resulting equations the various contributions of loops, trains, and tails [1] can be isolated. Loops are portions of the adsorbed chain in which only the first and the last monomer touch the wall, trains are portions in which all monomers are adsorbed, and tails are portions in which only the first monomer is in contact with the wall. Trains may therefore also be considered as a sequence of small loops with a size of the order of a monomer. Close to the wall small loops dominate the structure of the layer, whereas the concentration of the monomers in the tails is negligible. As the distance z from the wall increases the contribution of the loops to the overall monomer concentration profile decreases, but that of the tails increases. Due to this opposite behavior of the two profiles there should be a *crossover distance* z^*, which separates a loop-dominated regime adjacent to the wall ($z \ll z^*$) from a more distant regime ($z \gg z^*$), where the tails primarily determine the decay of the monomer profile. The division of the adsorbed layer in an inner and an outer part was suggested by the numerical solution of

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the self-consistent mean-field theory [7] and has also been observed in a recent Monte Carlo simulation [9].

This picture of the structure of an adsorbed layer has been substantiated theoretically by an extension of mean-field and scaling theories [10,11]. By going beyond the ground-state approximation [1] the contribution of the tails can be incorporated in the mean-field treatment. This refined theory, which is valid in the asymptotic limit of very long chains only, has been developed for monodisperse systems in the full concentration regime ranging from dilute to concentrated solutions. A central result is the natural appearance of the crossover distance z^* and the derivation of its chain length dependence [10]. This distance also appears as the pertinent length scale in the extended scaling theory which goes beyond the mean-field approach by calculating the spatial variation of loop and tail profiles under good solvent conditions [10,11]. Since the scaling theory yields the mean-field results when classical critical exponents [12] and the space dimension $d=4$ are used, and since the extended mean-field theory quantitatively agrees (in most cases) with the numerical solutions of the Scheutjens-Fleer theory [13], both approaches are indeed compatible and complement each other.

Therefore we use the extended mean-field and scaling theories in this paper to discuss the competitive adsorption of a polydisperse polymer sample. Polydispersity is modeled in the simplest–though experimentally studied [1,3]—fashion as a bidisperse mixture of chains of different length. Since we expect the adsorption preference to be most pronounced in dilute solution, we focus on this case in the present work, although more concentrated solutions could be treated by the same methods.

The paper is organized as follows. In the first part of Sec. II we summarize those results of the extended mean-field theory which are important for the subsequent analysis, apply them to the case of the bidisperse mixture, and compare our findings with the Scheutjens-Fleer theory. In the second part we drop the assumption that both chains considerably exceed the size of the adsorbed layer and discuss the case in which the short chains are much smaller than the layer's extent. Section III complements the mean-field treatment by developing the corresponding scaling theory. Section IV summarizes the main results and contains our conclusions.

II. MEAN-FIELD THEORY

The mean-field theory of the competitive adsorption of two polymers of different length starts from the following assumptions: The polymers are considered as ideal Gaussian chains with radii of gyration $R_1^2=(\ell^2/6)N_1$ and $R_2^2=(\ell^2/6)N_2$, where the statistical segment length ℓ [8] is assumed to be identical for both chains. These chains experience an average external potential $U_{\mathrm{ex}}/k_{\mathrm{B}}T$, which consists of two parts. The first part, $U_{\mathrm{w}}/k_{\mathrm{B}}T$, stems from the short-range interaction with the wall. The impenetrable wall is located at $z=0$ and is assumed to be structureless in the x,y directions so that the distance z from this wall is the only relevant length scale. The second part, $U_{\mathrm{int}}/k_{\mathrm{B}}T$, (approximately) accounts for the excluded-volume interaction with other chains. In mean-field theory the excluded-volume interaction is given by $U_{\mathrm{int}}(z)/k_{\mathrm{B}}T=vc(z)=\phi(z)$, where v is the excluded-volume parameter, $c(z)$ the total monomer concentration at distance z from the wall [8,10], i.e., $c(z)=c_1(z)+c_2(z)$, and $\phi(z)$ the total monomer volume fraction. Whereas U_{w} already vanishes at short distances from the wall, U_{int} tends towards the bulk volume fraction, $\phi^0=\phi_1^0+\phi_2^0$, if $z\to\infty$. Therefore it is convenient to define the origin of the potential as the bulk state so that

$$\begin{aligned} U_{\mathrm{ex}}(z)/k_{\mathrm{B}}T-\phi^0 &= U_{\mathrm{w}}(z)/k_{\mathrm{B}}T+\phi_1(z)+\phi_2(z)-\phi_1^0-\phi_2^0 \\ &:= U_{\mathrm{w}}(z)/k_{\mathrm{B}}T+U(z)/k_{\mathrm{B}}T \xrightarrow{z\to\infty} 0. \end{aligned} \tag{2.1}$$

In the following we measure all energies in units of $k_{\mathrm{B}}T$ and all lengths in units of $\ell/\sqrt{6}$.

One of the basic quantities to analyze the structure of the adsorbed layer is the partition function $\mathcal{Z}_i(n_i,z)$ of chain i with length n_i with one end at z and the other end lying anywhere between $z=0$ and $z=\infty$. This partition function obeys a Schrödinger-like equation [8,10]

$$\frac{\partial \mathcal{Z}_i}{\partial n_i}=\frac{\partial^2 \mathcal{Z}_i}{\partial z^2}-U(z)\mathcal{Z}_i \tag{2.2}$$

with the following boundary conditions. (i) $\mathcal{Z}_i(0,z)=1$ (the partition function of a monomer is normalized to 1). (ii) $\lim_{z\to\infty}\mathcal{Z}_i(n_i,z)=1$ (very far away from the wall the chains are free Gaussian chains, whose partition function is normalized). (iii) $\partial \ln\mathcal{Z}_i(n_i,z)/\partial z|_{z=0}=-1/b$. The third condition accounts for the effect of the short-range wall potential U_w at distances larger than its range which is assumed to be of the order of the monomer size. With this stipulation the detailed shape of the wall potential is not important. The only relevant parameter is the *extrapolation length b* which is inversely proportional to the excess energy per monomer with respect to the adsorption threshold. Therefore condition (iii) can *a fortiori* be applied to accurately describe the *universal mean-field properties* of the absorbed layer in the central and distal region, i.e., for $z>b$, in which we are particularly interested.

In addition to $\mathcal{Z}_i$ one can also introduce the partition functions of an adsorbed and a free chain, i.e., $\mathcal{Z}_{\mathrm{a},i}$ and $\mathcal{Z}_{\mathrm{f},i}$. By a *free chain* we mean a chain which does not touch the wall. Therefore $\mathcal{Z}_{\mathrm{f},i}$ satisfies Eq. (2.2) with the same boundary conditions except that the wall boundary condition (iii) has to be replaced by $\mathcal{Z}_{\mathrm{f},i}(n_i,0)=0$. On the other hand, an *adsorbed chain* touches the wall at least by one monomer. Since $\mathcal{Z}_i$ comprises both the adsorbed- and the free-chain configurations, it is possible to define $\mathcal{Z}_{\mathrm{a},i}$ as

$$\mathcal{Z}_{\mathrm{a},i}(n_i,z):=\mathcal{Z}_i(n_i,z)-\mathcal{Z}_{\mathrm{f},i}(n_i,z). \tag{2.3}$$

Taking the boundary conditions for the total and the free-chain partition functions into account, $\mathcal{Z}_{\mathrm{a},i}$ has the following properties: (i) $\mathcal{Z}_{\mathrm{a},i}(n_i,0)=\mathcal{Z}_i(n_i,0)$ and (ii) $\lim_{z\to\infty}\mathcal{Z}_{\mathrm{a},i}(n_i,z)=0$.

With these partition functions one can calculate the monomer concentration (i.e., volume fraction) profiles for loops and tails. Since the concentration profile $\phi_i(z)$ of a random-walk-like chain i is quite generally related to $\mathcal{Z}_i(n_i,z)$ by [8,10]

$$\phi_i(z)=\frac{\phi_i^0}{N_i}\int_0^{N_i}dn\,\mathcal{Z}_i(n,z)\mathcal{Z}_i(N_i-n,z), \tag{2.4}$$

the decomposition of $\mathcal{Z}_i(n_i,z)$ in an adsorbed and a free part immediately yields the profile of loops

$$\phi_{\mathrm{l},i}(z)=\frac{\phi_i^0}{N_i}\int_0^{N_i}dn\,\mathcal{Z}_{\mathrm{a},i}(n,z)\mathcal{Z}_{\mathrm{a},i}(N_i-n,z), \tag{2.5}$$

of tails

$$\phi_{\mathrm{t},i}(z)=\frac{2\phi_i^0}{N_i}\int_0^{N_i}dn\,\mathcal{Z}_{\mathrm{f},i}(n,z)\mathcal{Z}_{\mathrm{a},i}(N_i-n,z), \tag{2.6}$$

and of free chains

$$\phi_{\mathrm{f},i}(z)=\frac{\phi_i^0}{N_i}\int_0^{N_i}dn\,\mathcal{Z}_{\mathrm{f},i}(n,z)\mathcal{Z}_{\mathrm{f},i}(N_i-n,z). \tag{2.7}$$

In order to justify, for instance, the identification of Eq. (2.5) with the loop profile remember that $\mathcal{Z}_{\mathrm{a},i}(n,z)$ represents the partition function of an adsorbed chain with n monomers, whose one end is situated at z. Since an adsorbed chain touches the wall at least once and since $\mathcal{Z}_{\mathrm{a},i}(n,z)$ and $\mathcal{Z}_{\mathrm{a},i}(N_i-n,z)$ have a common end point at distance z from the wall, their product must describe a loop.

Using Eqs. (2.5) and (2.6) one can calculate the *adsorbance* Γ_i, i.e., the total amount of monomers per unit area in the adsorbed layer, by [10]

$$\Gamma_i=\int_0^\infty dz[\phi_{\mathrm{l},i}(z)+\phi_{\mathrm{t},i}(z)]=\Gamma_{\mathrm{l},i}+\Gamma_{\mathrm{t},i}\approx\Gamma_{\mathrm{l},i}. \tag{2.8}$$

The last (approximate) equality holds because the monomer profiles rapidly decay towards zero so that the major contribution comes from the loop-dominated regime $z<z^*$ [10]. Another way to estimate Γ_i is to integrate the density profile $\rho_{\mathrm{a},i}$ of the end monomers of the adsorbed chains. This density profile can also be expressed in terms of the partition function as [10]

$$\rho_{\mathrm{a},i}(z)=\frac{2\phi_i^0}{N_i}\mathcal{Z}_{\mathrm{a},i}(N_i,z) \tag{2.9}$$

so that

$$\Gamma_i=\phi_i^0\int_0^\infty dz\,\mathcal{Z}_{\mathrm{a},i}(N_i,z). \tag{2.10}$$

Based on these introductory considerations we want to discuss now the structure of an adsorbed layer consisting of two chains of different length, which is in equilibrium with a dilute solution. Under this condition one can neglect the bulk and the free-chain volume fraction in comparison to the local monomer concentration inside the layer so that the potential in Eq. (2.2) becomes

$$U(z)=\sum_{i=1,2}[\phi_{\mathrm{l},i}(z)+\phi_{\mathrm{t},i}(z)]. \tag{2.11}$$

For this situation two cases are distinguished: Case (a) refers to the situation when $R_1\gg R_2$ and both radii of gyration are much larger than the size λ of the adsorbed layer. On the other hand, in case (b) only R_1 is assumed to exceed λ, whereas $R_2\ll\lambda$.

A. Both chains are larger than the size of the layer: $\lambda\ll R_2\ll R_1$

Equation (2.2) has the general solution

$$\mathcal{Z}_i(n_i,z)=\sum_s K_s\psi_s(z)\exp[-E_s n_i], \tag{2.12}$$

where the normalized (real) eigenfunctions satisfy

$$-\frac{d^2\psi_s}{dz^2}+U(z)\psi_s=E_s\psi_s \tag{2.13}$$

and K_s is given by $K_s=\int_0^\infty dz\,\psi_s(z)$ [10]. If $U(z)$ were zero, Eq. (2.12), subject to the boundary conditions of the adsorption problem, would have one bound (i.e., adsorbed) state $E_0=-1/b^2$ and the corresponding eigenfunction would decrease exponentially with decay-length b. The presence of the repulsive potential $U(z)$ can only increase the ground-state energy without adding further bound states. Therefore we have $-1/b^2<E_0=:-\epsilon=-1/\lambda^2$ if $U(z)$ is nonzero. However, as in the case when $U(z)=0$, the ground-state eigenfunction decreases exponentially (if $z\gg\lambda$), but the decay length is now λ. Therefore λ measures the *size* of the adsorbed layer [10].

If $n_i\gg1$ one can separate the contribution of the adsorbed chains to $\mathcal{Z}_i$ from that of the free chains in the following way [10]:

$$\begin{aligned}\mathcal{Z}_i(n_i,z)&=K_0\psi_0(z)\exp[n_i\epsilon]+\int_0^\infty dq\,K(q)\psi(q,z)\\&\quad\times\exp[-n_iq^2]\\&=\mathcal{Z}_{\mathrm{a},i}(n_i,z)+\mathcal{Z}_{\mathrm{f},i}(n_i,z).\end{aligned} \tag{2.14}$$

In the limit $n_i\to\infty$, $\mathcal{Z}_{\mathrm{f},i}$ vanishes and the partition function of the adsorbed chains solely determines $\mathcal{Z}_i$. The *ground-state dominance approximation* [1] only works with $\mathcal{Z}_{\mathrm{a},i}$ also for finite chain length and thus ignores the contribution of the tails [see Eq. (2.6)]. Inserting Eq. (2.14) into Eq. (2.10) the adsorbance becomes

$$\Gamma_i=\phi_i^0K_0^2\exp[N_i\epsilon]. \tag{2.15}$$

The same result could have been obtained by balancing the chemical potential of the adsorbed layer with that of the dilute bulk (see Sec. III B for an application and [11]). Using Eqs. (2.14) and (2.15) in Eqs. (2.5) and (2.6) the profile of the loops is determined by [10]

$$\phi_{\mathrm{l},i}(z)=\psi_i^2:=\Gamma_{\mathrm{l},i}\psi_0^2(z)\approx\Gamma_i\psi_0^2(z) \tag{2.16}$$

with

$$-\frac{d^2\psi_i}{dz^2}+[U(z)+\epsilon]\psi_i=0;$$

$$\left.\frac{d\psi_i}{dz}\right|_0=-\frac{1}{b}\psi_i(0),\quad \lim_{z\to\infty}\psi_i(z)=0, \tag{2.17}$$

and that of the tails by

$$\phi_{\mathrm{t},i}(z)=B_i\psi_i(z)\varphi_i(z), \tag{2.18}$$

where

$$B_i=\frac{2\Gamma_i}{N_iK_i};\quad K_i\simeq\sqrt{\Gamma_i}K_0 \tag{2.19}$$

and

$$\varphi_i(z)=\int_0^{N_i}dn\,\mathcal{Z}_{\mathrm{f},i}(n,z)\exp[-n\epsilon] \tag{2.20}$$

with

$$-\frac{d^2\varphi_i}{dz^2}+[U(z)+\epsilon]\varphi_i=1;\quad \varphi_i(0)=0,\quad \lim_{z\to\infty}\varphi_i(z)\simeq\frac{1}{\epsilon}. \tag{2.21}$$

Since the functions, ψ_i and φ_i obey the same equations with the same boundary conditions for both chain lengths, we must have

$$\psi_1(z)=C_{12}\psi_2(z)\quad\text{and}\quad\varphi_1(z)=\varphi_2(z)=\varphi(z), \tag{2.22}$$

where C_{12} is a proportionality constant and φ_1 has to be equal to φ_2 due to the 1 on the right-hand side of Eq. (2.21). The physical reason for the latter property is that φ represents the partition function of a tail, which is the same for both short and long chains, since the density profiles of the end monomers, $\rho_{\mathrm{a},i}(z)$, are cut off exponentially if $z\gg\lambda$ and we assume $\lambda\ll R_2\ll R_1$ in this section. If one uses this ansatz together with Eqs. (2.16) and (2.18) in Eq. (2.11) the potential $U(z)$ is written as

$$\begin{aligned}U(z)&=\psi_1^2(z)+\psi_2^2(z)+B_1\psi_1(z)\varphi_1(z)+B_2\psi_2(z)\varphi_2(z)\\&=\psi^2(z)+B\psi(z)\varphi(z)\end{aligned} \tag{2.23}$$

with the definitions

$$\psi(z):=\sqrt{1+C_{12}^2}\,\psi_2(z)\quad\text{and}\quad B=\frac{1}{l^3}:=\frac{B_1C_{12}+B_2}{\sqrt{1+C_{12}^2}}. \tag{2.24}$$

As in Ref. [10] the last definition introduces a new length scale l which will turn out to be related to the crossover length z^* from the loop- to the tail-dominated regime. The functions ψ and φ satisfy Eqs. (2.17) and (2.21) with the potential (2.23). In this form the equations are identical to those for monodisperse chains so that the solutions derived in Ref. [10] can be used. Before applying these solutions to calculate the loop and tail profiles we want to determine and discuss the proportionality constant C_{12} in the next two subsections, since C_{12} is related to the ratio of the adsorbances.

1. Chain-length and concentration dependence of ϵ

Since the total adsorbance Γ is given by $\Gamma_1+\Gamma_2$, one finds by using Eqs. (2.8), (2.16), and (2.22),

$$C_{12}^2=\frac{\Gamma_1}{\Gamma_2}. \tag{2.25}$$

On the other hand, the ratio of the two adsorbances can also be expressed with the help of Eqs. (2.15) and (2.19) as

$$\left(\frac{\Gamma_1}{\Gamma_2}\right)^2=\frac{\phi_1^0}{\phi_2^0}\left(\frac{K_1}{K_2}\right)^2\exp[(N_1-N_2)\epsilon].$$

Taking into account that $K_i=\int_0^\infty dz\,\psi_i(z)$ another application of Eq. (2.22) yields $K_1/K_2=C_{12}$ so that

$$\frac{\Gamma_1}{\Gamma_2}=\frac{\phi_1^0}{\phi_2^0}\exp[(N_1-N_2)\epsilon]. \tag{2.26}$$

From this equation the chain length dependence of ϵ (i.e., of the size of the adsorbed layer) can be derived if one uses [see Eqs. (2.15), (2.19), and (2.25)]

$$\Gamma=\Gamma_1+\Gamma_2=\sqrt{\phi_1^0}K_1\exp[N_1\epsilon/2]\left[1+\frac{1}{C_{12}^2}\right]$$

and the results of Sec. II A 3 [see Eqs. (2.39)–(2.42)],

$$\Gamma=\frac{2}{b}\quad,\quad K_1=\frac{C_{12}}{\sqrt{1+C_{12}^2}}\sqrt{2}\ln\frac{l}{b}.$$

This yields for ϵ

$$N_1\epsilon=-\ln\left[\phi_1^0b^2\left(1+\frac{\phi_2^0}{\phi_1^0}\exp\left[-\left(1-\frac{N_2}{N_1}\right)N_1\epsilon\right]\right)\right], \tag{2.27}$$

where a term of order ln[ln(l/b)] has been ignored and Eq. (2.26) was applied again. This equation determines ϵ in a self-consistent fashion. Analytically, it can only be solved if $N_1=N_2=N$, with the result $N\epsilon=-\ln[(\phi_1^0+\phi_2^0)b^2]$. If $N_2<N_1$, an approximate formula may be obtained by assuming C_{12}^{-2} to be small so that the leading order expression, $N_1\epsilon=-\ln[\phi_1^0b^2]$, can be reinserted in the right-hand side of Eq. (2.27). Then

$$N_1\epsilon\approx-\ln\left[\phi_1^0b^2\left(1+\frac{\phi_2^0}{\phi_1^0}(\phi_1^0b^2)^{1-N_2/N_1}\right)\right]. \tag{2.28}$$

This equation (fortuitously) recovers the monodisperse result if $N_1=N_2$. Since the exponential function in Eq. (2.26) is always larger than or equal to 1, the assumption $C_{12}^{-2}<1$ is certainly justified if $\phi_2^0\leqslant\phi_1^0$, but also remains valid for $\phi_2^0>\phi_1^0$ as long as $N_2/N_1<\ln(\phi_2^0b^2)/\ln(\phi_1^0b^2)$. In the opposite case, $N_2/N_1>\ln(\phi_2^0b^2)/\ln(\phi_1^0b^2)$, one can again derive an approximate formula for ϵ, which coincides with Eq. (2.28) when interchanging the labels 1 and 2.

Equation (2.28) provides a criterion for the validity of the initial assumption that the thickness $\lambda=1/\epsilon^{1/2}$ of the adsorbed layer is smaller than the radius of gyration of the short chains. The condition $\lambda < R_2$ is satisfied as long as $N_2/N_1 > -1/\ln[\phi_1^0 b^2(1+(\phi_2^0/\phi_1^0)(\phi_1^0 b^2)^{1-N_2/N_1})]$. The opposite case where the short chains only have a weak affinity to the covered wall is considered in Sec. II B.

Inserting the approximate formula (2.28) in Eq. (2.26) one obtains for the ratio Γ_1/Γ_2

$$\frac{\Gamma_1}{\Gamma_2}=\frac{\phi_1^0}{\phi_2^0}\left[\phi_1^0 b^2\left(1+\frac{\phi_2^0}{\phi_1^0}(\phi_1^0 b^2)^{1-N_2/N_1}\right)\right]^{-(1-N_2/N_1)} \tag{2.29}$$

and for Γ_1/Γ and Γ_2/Γ

$$\frac{\Gamma_1}{\Gamma}=\left\{1+\frac{\phi_2^0}{\phi_1^0}\left[\phi_1^0 b^2\left(1+\frac{\phi_2^0}{\phi_1^0}(\phi_1^0 b^2)^{1-N_2/N_1}\right)\right]^{1-N_2/N_1}\right\}^{-1} \tag{2.30}$$

and

$$\frac{\Gamma_2}{\Gamma}=\left\{1+\frac{\phi_1^0}{\phi_2^0}\left[\phi_1^0 b^2\left(1+\frac{\phi_2^0}{\phi_1^0}\times(\phi_1^0 b^2)^{1-N_2/N_1}\right)\right]^{-(1-N_2/N_1)}\right\}^{-1}, \tag{2.31}$$

which yields for $N_1=N_2$

$$\frac{\Gamma_1}{\Gamma}=\frac{\phi_1^0}{\phi_1^0+\phi_2^0};\quad \frac{\Gamma_2}{\Gamma}=\frac{\phi_2^0}{\phi_1^0+\phi_2^0} \tag{2.32}$$

and for $N_2/N_1 \to 0$

$$\frac{\Gamma_1}{\Gamma}=\frac{1}{1+\phi_2^0 b^2(1+\phi_2^0 b^2)};\quad \frac{\Gamma_2}{\Gamma}=\frac{\phi_2^0 b^2(1+\phi_2^0 b^2)}{1+\phi_2^0 b^2(1+\phi_2^0 b^2)}. \tag{2.33}$$

Equations (2.30) and (2.31) show that the ratios of the adsorbances only depend on N_2/N_1 and not on the individual chain lengths. The same result is also found in the (numerical) solution of the Scheutjens-Fleer theory [5,6], with which we want to compare our analytical expressions in the next subsection.

2. Comparison with the Scheutjens-Fleer theory

In Ref. [6] Fleer discusses the structure of the adsorbed layer of a multicomponent mixture in the ground-state approximation and compares the results with the numerical solutions of self-consistent-field calculations. For the adsorption of two polymers differing only in chain length he finds for the total adsorbance [using our notation; see Eq. (20) of Ref. [6]]

$$\Gamma=\Gamma_1+\Gamma_2=B_{\rm F}[\phi_1^0\exp(N_1\epsilon)+\phi_2^0\exp(N_2\epsilon)],$$

where the factor $B_{\rm F}$ is taken to be 6 in numerical applications. Solving this equation for ϵ and setting $\Gamma=1$ [6] one obtains

$$N_1\epsilon=-\ln\left[B_{\rm F}\phi_1^0\left(1+\frac{1}{C_{12}^2}\right)\right],$$

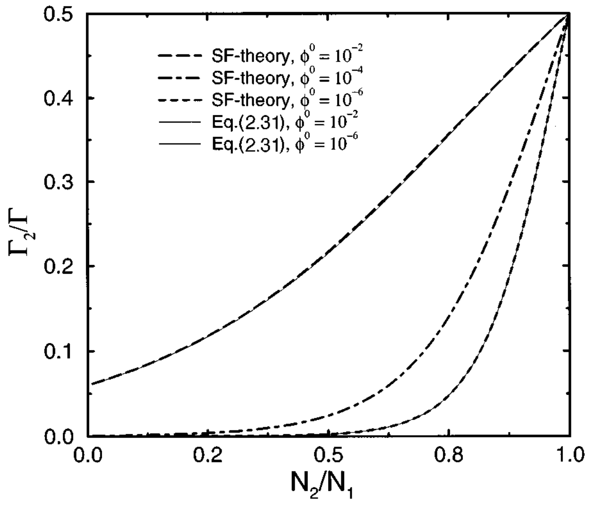

FIG. 1. Comparison of the Scheutjens-Fleer theory and Eq. (2.31). The figure shows the ratio of the adsorbance Γ_2 of the short chains to the total adsorbance Γ $(=\Gamma_1+\Gamma_2)$ as a function of the chain-length ratio N_2/N_1 when both chains have the same bulk volume fraction ϕ^0 and $b^2=6$. The thick lines correspond to the Scheutjens-Fleer (SF) theory [6], whereas the thin solid lines are the results of Eq. (2.31).

which coincides with Eq. (2.27) when identifying $B_{\rm F}$ with b^2. Using therefore $b^2=6$ and choosing furthermore $\phi_1^0=\phi_2^0=\phi^0=10^{-2},10^{-4},10^{-6}$, Eq. (2.31) can be compared with Fig. 1 of Ref. [6]. The result of this comparison is presented in Fig. 1. In the range of validity of Eq. (2.28) our approximate formula agrees very well with the numerical solution of the Scheutjens-Fleer theory. Since the dependence of Γ_2/Γ on N_2/N_1 is symmetric, this shows that Eq. (2.31) represents an adequate approximation for all relevant ratios of chain lengths. In addition, Fig. 1 also illustrates the adsorption preference of the long chains. As in experiments [1], the preference is more pronounced in more dilute solutions. At $\phi^0=10^{-6}$ a chain length difference of 20% reduces the contribution of the short chains to the total adsorbance to below 10%, whereas it is close to 40% if $\phi^0=10^{-2}$. Certainly, this latter volume fraction is an upper limit for a dilute polymer solution because ϕ^0 has to be smaller than the overlap concentration $\phi^*\approx(N_1^{d\nu-1}+N_2^{d\nu-1})^{-1}|_{d=4,\nu=1/2}=1/(N_1+N_2)$, which requires N_1 to be less than 100 if $\phi^0=10^{-2}$.

3. Concentration profiles of loops and tails

Since ψ_1 is proportional to ψ_2 and $\varphi_1=\varphi_2$, the loop and the tail concentration profiles of the two types of chains are proportional to each other inside the adsorption layer. Using Eqs. (2.16), (2.22), and (2.26) one finds for the loops

$$\phi_{l,2}(z)=\psi_2^2(z)=C_{12}^{-2}\psi_1^2(z)=\frac{\Gamma_2}{\Gamma_1}\phi_{l,1}(z), \tag{2.34}$$

and for the tails by virtue of Eqs. (2.18), (2.19), (2.22), (2.25), and $K_1/K_2=C_{12}$,

$$\phi_{t,2}(z)=B_2\psi_2(z)\varphi_2(z)=\frac{N_1\Gamma_2}{N_2\Gamma_1}\phi_{t,1}(z). \tag{2.35}$$

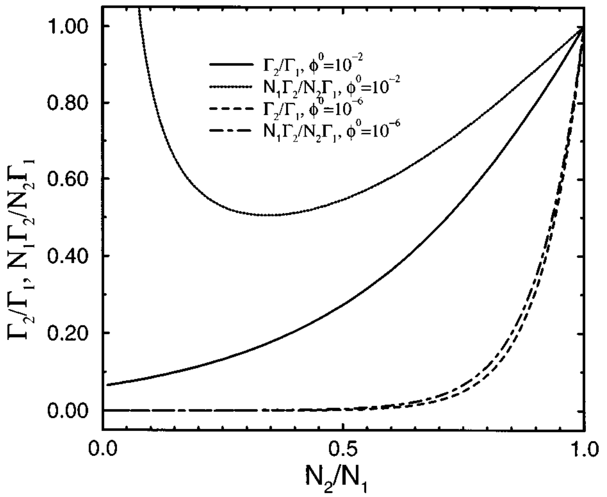

FIG. 2. Variation of the ratios Γ_2/Γ_1 and $N_1\Gamma_2/N_2\Gamma_1$ with the N_2/N_1. These ratios coincide with $\phi_{l,2}/\phi_{l,1}$ and $\phi_{t,2}/\phi_{t,1}$ due to Eqs. (2.34) and (2.35). In this figure the same bulk volume fractions, $\phi^0=10^{-2}$ and $\phi^0=10^{-6}$, have been used for both chains, and b^2 was taken to be 6.

The ratios of the two loop and chain profiles are plotted in Fig. 2 as a function of N_2/N_1 for $b^2=6$ and $\phi_1^0=\phi_2^0=\phi^0=10^{-2},10^{-6}$. As N_2/N_1 decreases, the long polymers progressively expel the short chains from the wall and form the majority of the loops. This expulsion is more successful in more dilute solutions. Whereas the ratio of the loop profiles (i.e., Γ_2/Γ_1) only decreases gradually for $\phi^0=10^{-2}$ and even stays finite for very small values of N_2/N_1, it is already completely negligible at $N_2/N_1\approx 0.5$ if $\phi^0=10^{-6}$. This behavior reflects the strong amplification of the adsorption preference by diluting the solution, which is also observed in experiments [1]. Contrary to Γ_2/Γ_1 the ratio of the tail profiles passes through a minimum upon decreasing N_2/N_1. This minimum is well pronounced [at (0.343, 0.505)] for $\phi^0=10^{-2}$, but very shallow and therefore invisible [at $(8.31\times 10^{-2}, 1.96\times 10^{-4})$] for $\phi^0=10^{-6}$, which is another consequence of the adsorption preference. The existence of this minimum and the subsequent increase of $\phi_{t,2}/\phi_{t,1}$ means that most of the tail monomers belong to short chains if N_2/N_1 becomes small.

In addition to these general relations between the profiles one can also immediately obtain their spatial variation, since the z dependence of ψ_i and φ_i is determined by that of ψ and φ. As mentioned above, these functions satisfy Eqs. (2.17) and (2.21), which are the same as in the monodisperse case [10]:

$$\psi(z)=\frac{\sqrt{2}}{z};\quad \varphi(z)=\frac{1}{3}z^2\ln\frac{l}{z}\quad \text{for } b\ll z\ll l, \tag{2.36}$$

$$\psi(z)=\frac{360l^3}{z^4};\quad \varphi(z)=\frac{z^2}{18}\quad \text{for } l\ll z\ll\lambda, \tag{2.37}$$

$$\psi(z)=\text{const}\times\frac{l^3}{\lambda^4}\exp\left[-\frac{z}{\lambda}\right];\quad \varphi(z)=\lambda^2\quad \text{for } \lambda\ll z. \tag{2.38}$$

[Formally, the monodisperse results of Ref. [10] can be recovered in the limit $C_{12}\to\infty$, which is realized either by $\phi_2^0\to 0$ or by $(N_1-N_2)\to\infty$.] The resulting concentration profiles for loops and tails are compiled in Table I. In a dilute solution the adsorbed chains also determine the overall concentration profile outside the adsorption layer up to a distance $D_i\approx N_i/\lambda>R_i$, whereas free chains dominate further away from the wall. Since the free chains are expelled from the layer, their profile gradually increases towards the bulk concentration for $z>\lambda$. Due to this opposite behavior of the adsorbed- and free-chain profiles the overall concentration profile of the short and the long chains exhibits a minimum. As in the monodisperse case this minimum is shallow and is predicted to lie at D_1 for the long and at D_2 for the short chains.

Equations (2.36)–(2.38) show that $\psi(z)$ rapidly decreases with increasing distance to the wall. Therefore the constants K_i and the adsorbances Γ_i can be approximated by Eq. (2.36) very well [10]. For K_i one obtains

$$K_1=\frac{C_{12}}{\sqrt{1+C_{12}^2}}\int_0^\infty dz\,\psi(z)\simeq\frac{C_{12}}{\sqrt{1+C_{12}^2}}\int_b^l dz\,\psi(z)$$

$$=\frac{C_{12}}{\sqrt{1+C_{12}^2}}\sqrt{2}\ln\frac{l}{b}, \tag{2.39}$$

$$K_2\simeq\frac{1}{\sqrt{1+C_{12}^2}}\sqrt{2}\ln\frac{l}{b}, \tag{2.40}$$

where the lower bound of the integral was replaced by b. This amounts to changing the variable z to $z+b$ for $z\ll l$,

TABLE I. Concentration profiles for loops and tails if both chains are much larger than the size of the layer, i.e., $\lambda\ll R_2\ll R_1$. The profiles are calculated from Eqs. (2.16) and (2.18) by virtue of Eqs. (2.36)–(2.43). Only the profiles for the long chains are given, since those of the short ones can then be deduced from Eqs. (2.34) and (2.35).

	$b\ll z\ll z^*$	$z^*\ll z\ll\lambda$	$\lambda\ll z\ll R_1,R_2$
$\phi_{l,1}$	$\frac{\Gamma_1}{\Gamma}\frac{2}{z^2}$	$\frac{\Gamma_1}{\Gamma}\frac{1800(z^*)^6}{z^8}$	$\frac{(\text{const})^2}{72}\times\frac{\Gamma_1}{\Gamma}\frac{(z^*)^6}{\lambda^8}\exp\left[-2\frac{z}{\lambda}\right]$
$\phi_{t,1}$	$\frac{1}{1+N_1/(N_2C_{12}^2)}\frac{4z}{(z^*)^3}\ln\left[\frac{z^*}{2^{1/2}3^{1/3}z}\right]$	$\frac{1}{1+N_1/(N_2C_{12}^2)}\frac{20}{z^2}$	$\frac{1}{1+N_1/(N_2C_{12}^2)}\frac{\text{const}}{\lambda^2}\times\exp\left[-\frac{z}{\lambda}\right]$

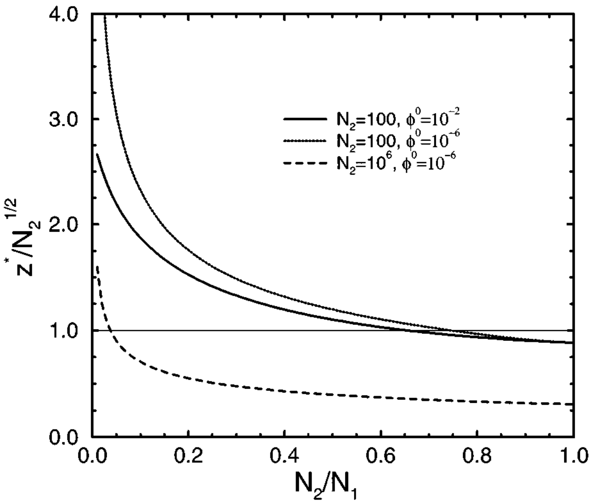

FIG. 3. Dependence of $z^*/N_2^{1/2}$ on N_2/N_1 for $N_2=10^2$, $\phi^0=10^{-2}$, and $N_2=10^2, 10^6$, $\phi^0=10^{-6}$. As before, we additionally use $b^2=6$.

which was justified in Ref. [10] to correctly account for the boundary condition of ψ close to the wall. Similarly, one finds for the adsorbances

$$\Gamma_1 \simeq \frac{C_{12}^2}{1+C_{12}^2}\int_b^l dz\,\psi(z)^2 \simeq \frac{C_{12}^2}{1+C_{12}^2}\,\frac{2}{b}, \tag{2.41}$$

$$\Gamma_2 \simeq \frac{1}{1+C_{12}^2}\,\frac{2}{b}, \tag{2.42}$$

which yields for the total adsorbance $\Gamma=\Gamma_1+\Gamma_2\simeq 2/b$. In this calculation a term of order $1/l$ was neglected, since the hitherto unspecified length scale l is strongly chain-length dependent. If one uses the above derived results for K_i and Γ_i in Eq. (2.19), l can be calculated from Eq. (2.24) as

$$l^3 = \frac{1}{2^{3/2}}\,\frac{N_1 N_2 b(1+C_{12}^2)}{N_2 C_{12}^2+N_1}\ln\frac{l}{b}.$$

Inserting the right-hand side of this equation into the argument of the logarithm and ignoring a factor of order $\ln[\ln(l/b)]$ one finds

$$\begin{aligned} l =: {} & \frac{1}{2^{1/2}3^{1/3}}z^* \\ \simeq {} & \frac{1}{2^{1/2}3^{1/3}}\left(\frac{N_2 b(1+C_{12}^2)}{1+N_2C_{12}^2/N_1}\ln\left[\frac{N_2(1+C_{12}^2)}{(1+N_2C_{12}^2/N_1)b^2}\right]\right)^{1/3}. \end{aligned} \tag{2.43}$$

The identification of l with the crossover length from the loop- to the tail-dominated regime is legitimate, since ψ is much larger than $B\varphi$ (and thus $\phi_l \gg \phi_t$) for $z \ll l$ [see Eq. (2.36)], whereas the opposite is true for $l \ll z$ [see Eq. (2.37)].

Equation (2.43) gives the chain-length and concentration dependence of z^*, which is exemplified in Fig. 3 for representative values of N_2 at $\phi_1^0=\phi_2^0=\phi^0=10^{-2}, 10^{-6}$. The choices $N_2=10^2$ for $\phi^0=10^{-2}$ and $N_2=10^6$ for $\phi^0=10^{-6}$ are certainly upper bounds if the solution is assumed to be dilute, i.e., if $\phi^0<\phi^*$ (see above). The figure shows that z^* increases with the chain-length disparity, the dilution (especially at small values of N_2/N_1), and the size of the short chains. If $N_2=10^2$, z^* rapidly becomes larger than R_2, whereas small values of N_2/N_1 are needed for z^* to exceed R_2 when $N_2=10^6$. This shows on the one hand that z^* is in general a large quantity so that the neglect of the term of order $1/l$ in Eqs. (2.41) and (2.42) is justified, and on the other hand that the length scales z^* and R_2 are not well separated in practice. Therefore it remains to be shown by computer simulations or experiments to what extent the above derived asymptotic laws are in fact observable.

B. One chain is smaller and one larger than the size of the layer: $R_2 \ll \lambda$, $\lambda \ll R_1$

The discussion of the preceding section showed that already a small difference in chain length can entail a substantial adsorption preference for the longer chains in a dilute solution. Since the chain length disparity is very large in the present case, one can thus assume that the properties of the adsorbed layer are exclusively defined by the long chains. They create the potential which determines the thermodynamic behavior of the short chains. Depending on the size of the short chains one can distinguish the following two cases:

$$U(z)=\phi_1(z)=\begin{cases} 2/z^2 & \text{for} \quad b \ll R_2 \ll z^* \\ 20/z^2 & \text{for} \quad z^* \ll R_2 \ll \lambda, \end{cases} \tag{2.44}$$

where the potential and the crossover length z^* are given by the monodisperse result [10] (i.e., by the limit $C_{12}\to\infty$). This choice therefore assumes a situation in which the small chains attempt to adsorb through a layer formed by the long polymers. In order to study the adsorption behavior under these circumstances one can no longer work with Eq. (2.14), since the given expressions for $\mathcal{Z}_{\rm a}$ and $\mathcal{Z}_{\rm f}$ are only valid asymptotically for $R_2 \gg \lambda$. Instead, one has to solve Eq. (2.2) using Eq. (2.44).

1. Short chains are smaller than z^*: $b \ll R_2 \ll z^*$

Introducing the Laplace transform, $\tilde{\mathcal{Z}}_2(E,z)$, with respect to n one can write Eq. (2.2) in the following form:

$$\frac{\partial^2 \tilde{\mathcal{Z}}_2}{\partial z^2} - [U(z)+E]\tilde{\mathcal{Z}}_2 = -1. \tag{2.45}$$

With $U(z)$ given by Eq. (2.44) this equation is solved for the total and the free-chain partition function in Appendix A. From these results one can derive the partition function of the adsorbed chains. For $U(z)=2/z^2$ the solution is [see Eq. (A12)]

$$\begin{aligned} \tilde{\mathcal{Z}}_{\rm a,2}(E,z) = {} & \frac{b}{z+b}\,\frac{1+\sqrt{E}(z+b)}{E(1+\sqrt{E}b)} \\ & \times \exp(-\sqrt{E}z)[1-{\rm Ei}(-\sqrt{E}b)\exp(\sqrt{E}b)], \end{aligned} \tag{2.46}$$

where ${\rm Ei}(x)$ is the exponential integral function [17]. Since $b \ll R_2$, $\sqrt{E}b \ll 1$ so that one can write

$$\frac{1+\sqrt{E}(z+b)}{E(1+\sqrt{E}b)}\approx\frac{1}{E}+\frac{z+b}{\sqrt{E}}$$

and

$$[1-\mathrm{Ei}(-\sqrt{E}b)\exp(\sqrt{E}b)]\approx-\ln\sqrt{E}b,$$

which then yields

$$\tilde{\mathcal{Z}}_{\mathrm{a},2}(E,z)\approx-\frac{b}{z+b}\ln\sqrt{E}b\left[\frac{1}{E}+\frac{z+b}{\sqrt{E}}\right]\exp[-\sqrt{E}z]. \tag{2.47}$$

Approximately, the inverse Laplace transform of Eq. (2.47) is

$$\mathcal{Z}_{\mathrm{a},2}(N_2,z)\approx\ln\frac{\sqrt{N_2}}{b}\,\frac{b}{z+b}\left[\mathrm{erfc}\left(\frac{z}{2\sqrt{N_2}}\right)+\frac{z+b}{\sqrt{\pi N_2}}\exp\left(-\frac{z^2}{4N_2}\right)\right]. \tag{2.48}$$

This approximation is correct in the vicinity of the wall, but becomes unsatisfactory in the cutoff region of the layer. Since the adsorbance is primarily determined by small loops close to the wall, one can use Eq. (2.48) to obtain the leading-order result for the adsorbance of the small chains [see Eq. (2.10)],

$$\Gamma_2=\phi_2^0\int_0^\infty dz\,\mathcal{Z}_{\mathrm{a},2}(N_2,z)=\phi_2^0 b\left[\ln\frac{\sqrt{N_2}}{b}\right]^2. \tag{2.49}$$

The same result would have also been expected on the basis of Eq. (2.15). Since $N_2\epsilon\ll1$ in the present case, $\Gamma_2\approx\phi_2^0 bK_2^2/2$, which yields Eq. (2.49) when replacing l by R_2 and ignoring the prefactor in Eq. (2.40). That the latter manipulations are legitimate comes from the fact that the ground-state approximation can be applied as long as $z<R_2$.

In addition to the adsorbance the concentration profile of the adsorbed chains can be calculated in the same approximation. Since the Laplace transform of Eq. (2.5) is proportional to $(\tilde{\mathcal{Z}}_{\mathrm{a},2})^2$, the approximate inverse transform of the square of Eq. (2.47) gives

$$\begin{aligned}\phi_{\mathrm{a},2}(z)\approx\phi_2^0\left[\ln\frac{\sqrt{N_2}}{b}\right]^2&\left[\left(\frac{b}{z+b}\right)^2\mathrm{erfc}\left(\frac{z}{\sqrt{N_2}}\right)\right.\\&-\frac{b^2}{N_2}\left[\frac{(z+b)^2-2b^2}{(z+b)^2}\right]\mathrm{erfc}\left(\frac{z}{\sqrt{N_2}}\right)\\&\left.+\frac{2b^2}{\sqrt{\pi N_2}}\left[\frac{z+2b}{(z+b)^2}\right]\exp\left(-\frac{z^2}{N_2}\right)\right],\end{aligned} \tag{2.50}$$

where erfc(x) is the complementary error function [17]. This equation shows that the concentration at the wall,

$$\phi_{\mathrm{a},2}(0)\approx\phi_2^0\left[\ln\frac{\sqrt{N_2}}{b}\right]^2, \tag{2.51}$$

increases with increasing chain length and that the concentration of the short chains is negligibly small at $z=R_2$, i.e.,

$$\phi_{\mathrm{a},2}(\sqrt{N_2})\approx\phi_2^0\left[\frac{b}{\sqrt{N_2}}\ln\frac{\sqrt{N_2}}{b}\right]^2\ll\phi_2^0. \tag{2.52}$$

On the other hand, free short chains from the bulk also enter the adsorption layer and contribute to the short-chain concentration profile. Qualitatively, one expects the free chains to penetrate up to a distance where the mesh size of the layer, which is essentially determined by the concentration profile of the long chains, becomes comparable to their radius of gyration R_2. Hence the concentration profile of the free chains is reduced by a factor of order 1 at $z=R_2$ with respect to the bulk value ϕ_2^0. Since additionally the concentration of the adsorbed chains is very small at $z=R_2$, the total concentration profile of the short chains should exhibit a minimum in the layer.

To test this idea let us calculate the (initial) decrease of the free-chain profile when entering the layer from the bulk. Using again the approximation $\sqrt{E}b\ll1$ one finds from Eqs. (A8), (A9), and (A11) (see Appendix A)

$$\begin{aligned}\tilde{\mathcal{Z}}_{\mathrm{f},2}(E,z)\approx\frac{1}{E}-\frac{1}{2E}\mathrm{Ei}(-\sqrt{E}z)&\left[1-\frac{1}{\sqrt{E}z}\right]\exp[\sqrt{E}z]\\&-\frac{1}{2E}\mathrm{Ei}(\sqrt{E}z)\left[1+\frac{1}{\sqrt{E}z}\right]\exp[-\sqrt{E}z].\end{aligned} \tag{2.53}$$

If one expands the exponential integral for large z the initial decrease of the partition function is

$$\tilde{\mathcal{Z}}_{\mathrm{f},2}(E,z)\overset{z\gg1}{\sim}\frac{1}{E}-\frac{2}{E^2z^2}$$

so that the free-chain profile [obtained from the inverse Laplace transform of $(\tilde{\mathcal{Z}}_{\mathrm{f},2})^2$, as before] asymptotically behaves as

$$\phi_{\mathrm{f},2}(z)\overset{z\gg1}{\sim}\phi_2^0\left[1-\frac{2}{z^2}N_2\right]. \tag{2.54}$$

This result can be rationalized as follows: The concentration profile of the free chains is proportional to the probability of entering the adsorbed layer, which is in turn proportional to the Boltzmann factor $\exp[-F/k_\mathrm{B}T]$. Since the free energy is (approximately) given by $F/k_\mathrm{B}T\approx N_2U(z)=2N_2/z^2$, we obtain

$$\phi_{\mathrm{f},2}(z)\approx\phi_2^0\exp[-N_2U(z)], \tag{2.55}$$

which gives Eq. (2.54) in the limit $z\gg1$. Numerically, Eq. (2.55) provides a good description of the behavior of $\phi_{\mathrm{f},2}$ up to the minimum of the total concentration profile so that one can use this equation and the leading expression for $\phi_{\mathrm{a},2}$ to assess z_{min}. Approximating therefore the total concentration profile by

$$\phi_2(z) \approx \phi_{\mathrm{a},2}(z) + \phi_{\mathrm{f},2}(z) \tag{2.56}$$

$$\approx \phi_2^0 \left[\left(\ln \frac{\sqrt{N_2}}{b} \right)^2 \left(\frac{b}{z+b} \right)^2 \mathrm{erfc}\left(\frac{z}{\sqrt{N_2}} \right) + \exp\left(-\frac{2N_2}{z^2} \right) \right] \tag{2.57}$$

yields $z_{\min} \propto R_2$, as expected. The ratio $z_{\min}/R_2$ is found to slowly decrease with increasing R_2. Additionally, Eq. (2.57) shows that almost total depletion occurs at the minimum for reasonable chain lengths.

2. Short chains are larger than z^*: $z^* \ll R_2 \ll \lambda$

In this regime the short chains also feel the potential for $z > z^*$. In order to derive the corresponding partition functions, $U(z) = 2/z^2$ must be replaced by $U(z) = 20/z^2$, but otherwise the same methods can be used to solve Eq. (2.45) (see Appendix A). The result for the partition function of the adsorbed chains is [see Eq. (A16)]

$$\tilde{\mathcal{Z}}_{\mathrm{a},2}(E,z) = A_{\mathrm{a},-} \left[1 + \frac{10}{E^{1/2}z} + \frac{45}{Ez^2} + \frac{105}{E^{3/2}z^3} + \frac{105}{E^2 z^4} \right] \times \exp[-\sqrt{E}z]. \tag{2.58}$$

Formally, the integration constant in Eq. (2.58) is given by the difference of the integration constants for the total and the free-chain partition functions, i.e., by $A_{\mathrm{a},-} = A_- - A_{\mathrm{f},-}$. However, A_- and $A_{\mathrm{f},-}$ cannot be determined via the conditions (A2) and (A3) because $z \gg z^* \gg b$. To fix $A_{\mathrm{a},-}$ nevertheless one can argue that an adsorbed chain in the regime $z \ll R_2$ does not feel whether its radius of gyration is smaller or larger than λ so that the results of Sec. II A should be applicable. This amounts to requiring the small z behavior of Eq. (2.58) to equal [see Eqs. (2.14), (2.37), and (2.40)]

$$\mathcal{Z}_{\mathrm{a},2}(N_2,z) \approx \frac{b}{2} K_2 \psi(z) \overset{z^* \ll z}{\sim} 30 \left[\ln \frac{z^*}{b} \right] \frac{b(z^*)^3}{z^4},$$

which yields

$$A_{\mathrm{a},-} = \frac{2}{7} \left[\ln \frac{z^*}{b} \right] b(z^*)^3 E. \tag{2.59}$$

If this result is inserted in Eq. (A1) one can calculate the contribution of the region $z^* \ll z$ to the adsorbance, i.e.,

$$\Gamma_2^{z^* \ll z} = \phi_2^0 \int_{z^*}^{\infty} dz\, \mathcal{Z}_{\mathrm{a},2}(N_2,z).$$

Integrating Eq. (2.58) first and performing then the inverse Laplace transform one obtains

$$\Gamma_2^{z^* \ll z} \approx 10 \phi_2^0 b \ln \frac{z^*}{b}. \tag{2.60}$$

To estimate also the contribution from the region $z \ll z^*$ the results of the preceding subsection cannot be applied directly, since the integration constants were determined by assuming z^* to be infinite. However, one can proceed as before and fix the integration constant for the partition function of the adsorbed chains by requiring $\mathcal{Z}_{\mathrm{a},2}$ to equal [see Eqs. (2.14), (2.36), and (2.40)]

$$\mathcal{Z}_{\mathrm{a},2}(N_2,z) \approx \frac{b}{2} K_2 \psi(z) \overset{z \ll z^*}{\sim} b \ln \frac{z^*}{b} \frac{1}{z},$$

which gives

$$A_{\mathrm{a},-} = b \left[\ln \frac{z^*}{b} \right] \frac{1}{E}. \tag{2.61}$$

Laplace transformation and integration then yield

$$\Gamma_2^{z \ll z^*} \approx \phi_2^0 b \left[\ln \frac{z^*}{b} \right]^2. \tag{2.62}$$

With this result the total adsorbance is given by

$$\Gamma_2 \approx \Gamma_2^{z \ll z^*} + \Gamma_2^{z^* \ll z} \approx \phi_2^0 b \ln \frac{z^*}{b} \left[\ln \frac{z^*}{b} + 10 \right] \approx \Gamma_2^{z \ll z^*}. \tag{2.63}$$

As in the previous case, this equation coincides with the expectation from Sec. II A. This could have been anticipated because the arguments given in the discussion following Eq. (2.49) also apply to the present case where $R_2 > z^*$. If $R_2 > z^*$, the integral of the ground-state eigenfunction is dominated by the vicinity of z^* so that $\Gamma_2 \approx \phi_2^0 b \ln^2(z^*/b)$ to leading order. Similarly, one expects that the total concentration profile is dominated by the ground state, i.e., $\phi_2(z) \approx \phi_{\mathrm{a},2}(z) \propto z^{-2}$, close to the wall and exhibits a minimum, the position of which is proportional to R_2.

III. SCALING APPROACH

Whereas the mean-field theory is only practically relevant for (nearly) ideal solutions, the aim of the scaling theory is to extend the description to good solvents, where the excluded-volume interaction is important. This section therefore reconsiders the structural properties of the adsorbed layer by scaling arguments. The first subsection examines the loop and tail profiles, whereas the second discusses the adsorbances and related quantities.

A. Loop and tail profiles

Originally, the scaling theory of polymer adsorption was developed by de Gennes [14]. The theory starts from the assumption that the structure of the adsorbed layer is *locally* identical to that of a semidilute bulk solution. The structure of a semidilute solution is characterized by the blob size ξ which depends on concentration as $\xi \sim \phi^{-\nu/(d\nu-1)}$ [15], where d is the space dimension and ν is the critical exponent of the order-parameter correlation length ($\nu = 0.588$ in $d = 3$ for polymers [12]). Since ϕ decreases with increasing distance, z, to the wall, ξ must increase with z. As long as $b < z < \lambda < R_2, R_1$, de Gennes suggested that it is the only relevant length scale so that $\xi(z) \simeq z \simeq n^{\nu}$ [14]. Hence

$$\phi(z) \sim z^{-d+1/\nu}, \tag{3.1}$$

which gives back the mean-field result, $\phi(z) \sim z^{-2}$, for $d=4$ and $\nu=1/2$ (see Table I).

However, the preceding discussion based on mean-field theory suggests that there exists an intermediate length scale z^* and that the power-law behavior of Eq. (3.1) should only be observed if either $z<z^*$ or $z>z^*$. If one assumes that the mean-field predictions remain qualitatively valid under good solvent conditions, for instance, that the loops also dominate close to the wall, one obtains

$$\phi(z) \approx \phi_{\mathrm{l}}(z) = \phi_{\mathrm{l},1}(z) + \phi_{\mathrm{l},2}(z) \sim z^{-d+1/\nu} \quad .$$

Since R_1 and R_2 are larger than the thickness of the layer, the loop and tail partition functions of the short and the long chains are identical for $z<\lambda$. This implies for the loop concentration profiles of both chains

$$\phi_{\mathrm{l},1}(z) \propto \phi_{\mathrm{l},2}(z) \sim z^{-d+1/\nu} \quad \text{if} \quad z<z^*. \tag{3.2}$$

Since $\phi_{\mathrm{l},1}$ is proportional to $\phi_{\mathrm{l},2}$, the condition $\Gamma \approx \int_0^\infty dz\, \phi_l(z)$ quite generally yields

$$\phi_{\mathrm{l},2}(z) = \frac{\Gamma_2}{\Gamma_1} \phi_{\mathrm{l},1}(z),$$

i.e., Eq. (2.34). Additionally, a comparison of Eq. (3.2) with the scaling theory of Refs. [10,11] reveals that the individual loop profiles behave as in the monodisperse case so that the results of Refs. [10,11] can be used. More precisely, this implies that the tail profiles are given by

$$\phi_{\mathrm{t},1}(z) \sim \frac{\Gamma_1}{N_1} z^{-1+1/\nu} \quad \text{and} \quad \phi_{\mathrm{t},2}(z) \sim \frac{\Gamma_2}{N_2} z^{-1+1/\nu}, \tag{3.3}$$

if $z<z^*$, which yields the mean-field result for $\nu=1/2$. Equation (3.3) also shows that

$$\phi_{\mathrm{t},2}(z) = \frac{N_1 \Gamma_2}{N_2 \Gamma_1} \phi_{\mathrm{t},1}(z),$$

which coincides with Eq. (2.35). Therefore Eqs. (2.34) and (2.35) do not depend on the mean-field approximation, but are quite general results.

Since the loop profile decreases and the tail profile increases with increasing z, there must be an intersection point. This intersection point defines the (up to now undetermined) crossover length z^* [10,11]. Requiring the total loop and tail profiles to be equal at z^*, i.e., $\phi_l(z^*) = \phi_t(z^*)$, Eqs. (3.2) and (3.3) yield

$$z^* \simeq \left[\frac{N_2(1+C_{12}^2)}{(1+N_2 C_{12}^2/N_1)\Gamma} \right]^{1/(d-1)}, \tag{3.4}$$

where $C_{12}^2 = \Gamma_1/\Gamma_2$, as before. Up to a logarithmic factor and numerical constants this result agrees with Eq. (2.43) when choosing $d=4$.

The opposite behavior of the loop and the tail profiles suggests that (as in mean-field theory) the loops only dominate as long as $z<z^*$, whereas the total concentration profile is determined by the tail contribution, i.e., $\phi(z) \approx \phi_{\mathrm{t}}(z) = \phi_{t,1}(z) + \phi_{\mathrm{t},2}(z)$, if $z>z^*$. The self-similar structure of the total concentration profile then entails in analogy to Eq. (3.2)

$$\phi_{\mathrm{t},1}(z) \sim \frac{\Gamma_1}{N_1} (z^*)^{-1+1/\nu} \left[\frac{z}{z^*} \right]^{-d+1/\nu}$$

and

$$\phi_{\mathrm{t},2}(z) \sim \frac{\Gamma_2}{N_2} (z^*)^{-1+1/\nu} \left[\frac{z}{z^*} \right]^{-d+1/\nu}, \tag{3.5}$$

where the prefactors were determined by requiring the tail profiles for $z>z^*$ to equal those for $z<z^*$ at $z=z^*$. Since the profiles for the short and the long chains are proportional to each other, the results of the monodisperse case can be applied. This implies for the loop profiles in the region $z>z^*$ [10,11]

$$\phi_{\mathrm{l},1}(z) \propto \phi_{\mathrm{l},2}(z) \sim (z^*)^{-d+1/\nu} \left[\frac{z}{z^*} \right]^{(1-\gamma-2d\nu)/\nu}, \tag{3.6}$$

where γ is the critical exponent of the susceptibility ($\gamma=1.162$ for polymers in $d=3$ [12]). Equation (3.6) coincides with Eq. (3.2) at $z=z^*$. These results for $z<z^*$ and $z>z^*$ show that the total loop and tail profiles may be written in terms of a scaling function as $\phi_{\mathrm{l,t}}(z) = z^{-d+1/\nu} \tilde{\phi}_{\mathrm{l,t}}(z/z^*)$ and that z^* is the relevant length scale in the universal central region of the adsorbed layer.

The preceding discussion applies if R_1 and R_2 are both larger than the thickness of the adsorption layer. If $R_2<\lambda$, the short chains are almost completely expelled from the layer and the lengths z^* and λ essentially agree with those of a monodisperse layer which is formed by the long chains only. In this case the previous formulas for the concentration profiles of the short chains remain valid up to the cutoff length R_2.

Additionally, the total concentration profiles of both the short and long chains are expected to be nonmonotonic, as in mean-field theory.

B. Adsorbances and related quantities

The adsorbances of the two polymer species are determined by the equilibrium condition between the adsorbed layer and the dilute bulk solution, i.e., by the equality of the chemical potentials $\mu_{\mathrm{ads},i}$ and $\mu_{\mathrm{sol},i}$. To calculate the chemical potentials an expression for the respective free energies is needed. Since there are ϕ_i^0/N_i indistinguishable self-avoiding polymers of species i in the bulk solution, the free energy is given by

$$F_{\mathrm{sol},i}(\phi_i^0, N_i) = F_{\mathrm{sol},i}(\phi_i^0) + \frac{\phi_i^0}{N_i} \ln\left(\frac{\phi_i^0}{N_i e} \right) - \frac{\phi_i^0}{N_i} \ln(N_i^{\gamma-1}), \tag{3.7}$$

where the first term is a chain-length independent contribution which contains the monomer partition function, the second term accounts for the entropy of mixing, and the last term, the so-called *enhancement factor*, originates from the partition function of a single self-avoiding chain. Equation (3.7) implies for the chemical potential

$$\mu_{\text{sol},i}=\frac{dF_{\text{sol},i}}{d\phi_i^0}+\frac{1}{N_i}\ln\left(\frac{\phi_i^0}{N_i}\right)-\frac{1}{N_i}\ln(N_i^{\gamma-1}). \qquad (3.8)$$

The chemical potential of the adsorbed layer is more difficult to estimate due to the contribution of the loops. In the interfacial region there are Γ_i/N_i indistinguishable self-avoiding chains of species i, each of which has two tails and an *unknown* number of loops. Due to this unknown number the contribution of the loops cannot be estimated from the loop partition function contrary to that of the tails. In analogy to Refs. [10,11] one finds that the partition function of a tail is given by

$$\mathcal{Z}_{\text{t},i}(n)\sim n^{(\gamma-\nu[d-2])/2-1} \quad \text{for} \quad i=1,2; \quad z<z^* \qquad (3.9)$$

and by

$$\mathcal{Z}_{\text{t},i}(n)\sim (n^*)^{(\gamma-\nu[d-2])/2-1}\left[\frac{n}{n^*}\right]^{-\nu(d-1)-1}$$
$$\text{for} \quad i=1,2; \quad z>z^*, \qquad (3.10)$$

where $n^*\simeq(z^*)^{1/\nu}$. The prefactor for $z>z^*$ is determined in such a way that Eqs. (3.9) and (3.10) coincide for $n=n^*$. Using these results one obtains for the chemical potential of the two tails of a chain

$$\mu_{\text{t},i}(\Gamma_i,N_i)\simeq-\frac{1}{N_i}\ln\left(\int_0^{N_i}dn\,\mathcal{Z}_{\text{t},i}(n)\right)^2$$
$$\simeq-\frac{1}{N_i}\ln(n^*)^{\gamma-\nu(d-2)}, \qquad (3.11)$$

since the integral is dominated by the vicinity of n^* if $z^*<R_i$.

To estimate also the loop contribution to the free energy one can assume that it primarily arises from the small loops inside the proximal region $z<b$. As the adsorbed layer is (usually) fairly dense in the vinicity of the wall, one can further assume that the (vanishingly small) loops behave as if they formed *a two-dimensional melt*. For two-dimensional melts Duplantier showed that, though the exponent ν takes the classical value $\nu=1/2$, the susceptibility exponent γ_{2d} is nontrivial, i.e., $\gamma_{2d}=19/16$ [16]. Taking this result into account for the enhancement factor the free energy of the loops becomes in analogy to Eq. (3.7)

$$F_{\text{l},i}(\Gamma_i,N_i)\approx F_{\text{ads},i}(\Gamma_i)+\frac{\Gamma_i}{N_i}\ln\left(\frac{\Gamma_i}{N_i\text{e}}\right)-\frac{\Gamma_i}{N_i}\ln(N_i^{\gamma_{2d}-1}), \qquad (3.12)$$

where $F_{\text{ads},i}$ is a chain-length independent contribution related to the partition function of an adsorbed monomer. This yields for the chemical potential of the adsorbed layer

$$\mu_{\text{ads},i}=\frac{dF_{\text{ads},i}}{d\Gamma_i}+\frac{1}{N_i}\ln\left(\frac{\Gamma_i}{N_i}\right)-\frac{1}{N_i}\ln(N_i^{\gamma_{2d}-1})$$
$$-\frac{1}{N_i}\ln(n^*)^{\gamma-\nu(d-2)}. \qquad (3.13)$$

Requiring now that $\mu_{\text{ads},1}=\mu_{\text{sol},1}$ and $\mu_{\text{ads},2}=\mu_{\text{sol},2}$, and substracting the resulting equations the ratio Γ_1/Γ_2 can be expressed as

$$\frac{\Gamma_1}{\Gamma_2}=\frac{\phi_1^0}{\phi_2^0}\left(\frac{N_1}{N_2}\right)^{\gamma_{2d}-\gamma}\exp[(N_1-N_2)\epsilon], \qquad (3.14)$$

where $\epsilon=(dF_{\text{sol},1}/d\phi_1^0)-(dF_{\text{ads},1}/d\Gamma_1)=(dF_{\text{sol},2}/d\phi_2^0)-(dF_{\text{ads},2}/d\Gamma_2)$. This equation coincides with Eq. (2.26) in the mean-field limit (i.e., $\gamma_{2d}\rightarrow\gamma=1$). However, also in good solvents the chain-length-dependent prefactor is always close to 1 for any reasonable choice of the ratio N_1/N_2, since $\gamma_{2d}-\gamma\approx0.0255$. This means that the effect of the excluded-volume interaction is to renormalize the adsorption energy, whose chain-length and concentration dependence we want to estimate now.

To calculate this dependence one can follow the lines of argument of Sec. II A 1. In addition to the ratio Γ_1/Γ_2 also one of the individual adsorbances, say Γ_1, is needed. Using the equilibrium condition, $\mu_{\text{ads},1}=\mu_{\text{sol},1}$, again one obtains

$$\Gamma_1=(\phi_1^0)^aN_1^b\left[1+\frac{\Gamma_2N_1}{\Gamma_1N_2}\right]^{-c}\exp[aN_1\epsilon], \qquad (3.15)$$

and from that by virtue of $\Gamma=\Gamma_1(1+\Gamma_2/\Gamma_1)$

$$N_1\epsilon=-\frac{1}{a}\ln\Bigg[\frac{(\phi_1^0)^a}{\Gamma}N_1^b\left(1+\frac{\phi_2^0}{\phi_1^0}\left(\frac{N_2}{N_1}\right)^{\gamma_{2d}-\gamma}\right.$$
$$\left.\left.\times\exp\left[-\left(1-\frac{N_2}{N_1}\right)N_1\epsilon\right]\right)\right]$$
$$+\frac{1-a}{a}\ln\left(1+\frac{\phi_2^0}{\phi_1^0}\left(\frac{N_2}{N_1}\right)^{\gamma_{2d}-\gamma-1}\right.$$
$$\left.\times\exp\left[-\left(1-\frac{N_2}{N_1}\right)N_1\epsilon\right]\right), \qquad (3.16)$$

where the abbreviations $a=\nu(d-1)/(\gamma+\nu)$, $b=(\gamma-\nu(d-2)+\nu(d-1)[\gamma_{2d}-\gamma])/(\gamma+\nu)$, and $c=(\gamma-\nu[d-2])/(\nu+\gamma)$ were introduced. Since $\gamma=1.162$ and $\nu=0.588$ in $d=3$, the exponents a, b, and c have the values $a\approx0.672$, $b\approx0.345$, and $c\approx0.328$, whereas $a=1$, and $b=c=0$ in the mean-field limit, i.e., if $\nu=1/2$, $\gamma_{2d}=\gamma=1$, and $d=4$. For the latter choices of a, b, and c, Eq. (3.16) gives back the mean-field result (2.27).

As in mean-field theory [see Eq. (2.27)] the adsorption energy has to be determined self-consistently. In order to derive an approximate expression for ϵ let us assume that

$$\frac{\phi_2^0}{\phi_1^0}\left(\frac{N_2}{N_1}\right)^{\gamma_{2d}-\gamma-1}\exp\left[-\left(1-\frac{N_2}{N_1}\right)N_1\epsilon\right]\ll1,$$

which requires $\phi_2^0/\phi_1^0\leqslant N_2/N_1\leqslant1$. Then the leading contribution of Eq. (3.16) is

$$N_1\epsilon=-\ln\left[\frac{\phi_1^0}{\Gamma^{1/a}}N_1^{b/a}\right], \qquad (3.17)$$

which, when inserted in Eq. (3.16), yields

$$N_1\epsilon \approx -\frac{1}{a}\ln\left[\frac{(\phi_1^0)^a}{\Gamma}N_1^b\left(1+\frac{\phi_2^0}{\phi_1^0}\left(\frac{N_2}{N_1}\right)^{\gamma_{2d}-\gamma}\right.\right.$$
$$\left.\left.\times\left[\frac{\phi_1^0}{\Gamma^{1/a}}N_1^{b/a}\right]^{1-N_2/N_1}\right)\right]. \tag{3.18}$$

This equation coincides with Eq. (2.27) in the mean-field limit, but depends explicitly on N_1 (and not only on N_2/N_1) under good solvent conditions. If Eq. (3.18) is inserted in Eq. (3.14) one obtains for the ratio of the adsorbances

$$\frac{\Gamma_1}{\Gamma_2}=\frac{\phi_1^0}{\phi_2^0}\left(\frac{N_1}{N_2}\right)^{\gamma_{2d}-\gamma}\left[\frac{(\phi_1^0)^a}{\Gamma}N_1^b\left(1+\frac{\phi_2^0}{\phi_1^0}\left(\frac{N_2}{N_1}\right)^{\gamma_{2d}-\gamma}\right.\right.$$
$$\left.\left.\times\left[\frac{\phi_1^0}{\Gamma^{1/a}}N_1^{b/a}\right]^{1-N_2/N_1}\right)\right]^{-(1-N_2/N_1)/a}, \tag{3.19}$$

which yields for $N_2/N_1=1$

$$\frac{\Gamma_1}{\Gamma_2}=\frac{\phi_1^0}{\phi_2^0},$$

and for $N_2/N_1\rightarrow 0$

$$\frac{\Gamma_1}{\Gamma_2}=\left\{\frac{\phi_2^0}{\Gamma^{1/a}}\left(\frac{N_2}{N_1}\right)^{\gamma_{2d}-\gamma}\right.$$
$$\left.\times N_1^{b/a}\left[1+\frac{\phi_2^0}{\Gamma^{1/a}}\left(\frac{N_2}{N_1}\right)^{\gamma_{2d}-\gamma}N_1^{b/a}\right]^{1/a}\right\}^{-1}.$$

Using the latter result the ratios Γ_1/Γ and Γ_2/Γ can be expressed as

$$\frac{\Gamma_1}{\Gamma}=\left\{1+\frac{\phi_2^0}{\Gamma^{1/a}}\left(\frac{N_2}{N_1}\right)^{\gamma_{2d}-\gamma}N_1^{b/a}\left[1+\frac{\phi_2^0}{\Gamma^{1/a}}\left(\frac{N_2}{N_1}\right)^{\gamma_{2d}-\gamma}N_1^{b/a}\right]^{1/a}\right\}^{-1}, \tag{3.20}$$

$$\frac{\Gamma_2}{\Gamma}=\frac{(\phi_2^0/\Gamma^{1/a})(N_2/N_1)^{\gamma_{2d}-\gamma}N_1^{b/a}[1+(\phi_2^0/\Gamma^{1/a})(N_2/N_1)^{\gamma_{2d}-\gamma}N_1^{b/a}]^{1/a}}{1+(\phi_2^0/\Gamma^{1/a})(N_2/N_1)^{\gamma_{2d}-\gamma}N_1^{b/a}[1+(\phi_2^0/\Gamma^{1/a})(N_2/N_1)^{\gamma_{2d}-\gamma}N_1^{b/a}]^{1/a}}, \tag{3.21}$$

if $N_2/N_1\rightarrow 0$, whereas the mean-field results [i.e., Eq. (2.32)] are recovered for $N_1=N_2$.

If the radius of gyration of the short chains is smaller than the size of the layer, but larger than z^*, the discussion presented above remains valid. However, if $R_2<z^*$, the contribution of the tails to the chain's free energy must be calculated from Eq. (3.9) alone. In analogy to Eq. (3.11) one then finds

$$\frac{N_2}{\Gamma_2}F_{t,2}(\Gamma_2,N_2)\simeq -2\ln\left(\int_0^{N_2}dn[n^{(\gamma-\nu[d-2])/2-1}]\right)$$
$$\simeq -\ln N_2^{\gamma-\nu(d-2)}. \tag{3.22}$$

Determining from that the free energy of the adsorbed layer and balancing the resulting chemical potential with that of the bulk solution, one obtains for the adsorbance of the short chains

$$\Gamma_2=\phi_2^0N_2^{\gamma_{2d}-\nu[d-2]}\exp[N_2\epsilon]\simeq\phi_2^0N_2^{\gamma_{2d}-\nu[d-2]}, \tag{3.23}$$

where we assumed $N_2\epsilon\ll 1$ as in mean-field theory. Since the value of the exponent in this equation is numerically close to $\nu=0.588$ [i.e., $\gamma_{2d}-\nu(d-2)\approx 0.6$ in $d=3$], the adsorbance is approximately proportional to R_2 in this case.

IV. SUMMARY AND CONCLUDING REMARKS

This paper discusses equilibrium properties of the competitive adsorption between two polymer species of different length by mean-field and scaling theories. The employed theoretical methods are based on recent developments [10,11] which extend the mean-field and scaling approaches to properly account for the contribution of loops and tails to the overall concentration profile. A central result of this extension is the appearance of a new length scale z^* which separates a loop-dominated regime closer to the wall from a tail-dominated one farther away from the wall. This length scale is also found in the present work. It increases with the size ratio of the short and the long chains, the dilution, and the chain length N_2 of the short chains.

The main results of the paper may be summarized as follows. (i) Long chains are adsorbed preferentially, and the adsorption preference becomes strongly reinforced when diluting the solution or decreasing the ratio N_2/N_1. (ii) If both chains are larger than the size, λ, of the adsorbed layer the adsorption preference is mainly due to the linear increase of the adsorption free energy per chain with chain length. The details of the concentration profiles only have a minor influence [see Eqs. (2.26) and (3.14)]. In mean-field theory the ratio of the adsorbances, Γ_1/Γ_2, depends only on N_2/N_1 [see Eq. (2.29)], whereas an additional absolute dependence on N_1 is found by the scaling analysis [see Eq. (3.19)]. The loop- and tail-concentration profiles of the short and the long chains are proportional to each other inside the adsorption layer and exhibit a (shallow) minimum outside the layer. The position of this minimum differs for both chain types and is larger than the respective radius of gyration. It is located at $D_1\propto N_1\lambda^{1-1/\nu}>D_2\propto N_2\lambda^{1-1/\nu}$ [19]. (iii) If the short chains are smaller than the size of the adsorbed layer (which is then assumed to be formed by the long chains only), but larger than z^* the preceding discussion remains valid except that the concentration profiles of the short chains are cut off at the radius of gyration R_2. Therefore the minimum of the short chains' total profile moves inside the adsorption layer and becomes more pronounced as N_2 decreases. Additionally, as in the case where both chains are larger than λ, scaling theory predicts that the adsorbance of the short chains is almost independent of N_2, but depends explicitly on N_1 under good solution conditions. Approximately, it is proportional to $\phi_0^2 N_1^{1/2}$ [see Eq. (3.21)]. This scaling result is in contrast to the mean-field prediction which yields a logarithmic dependence [see Eq. (2.63)]. (iv) If the short chains are smaller than z^* the minimum of the total concentration profile is strongly pronounced and the adsorbance shrinks to roughly $\Gamma_2 \approx \phi_0^2 R_2$ [see Eq. (3.23)]. Again, the explicit dependence of Γ_2 on R_2 is a scaling prediction, whereas only a logarithmic dependence is expected from mean-field theory [see Eq. (2.49)]. (v) The excess amount of monomers in the interfacial region is dominated by the immediate vicinity of the wall, i.e., by the loops, irrespective of whether R_2 is smaller or larger than the size of the adsorbed layer. Therefore our mean-field results compare very well with the numerical solution of the Scheutjens-Fleer theory.

In principle, it is possible to extend the present theory to continuous polydispersity distributions, as they often occur in experiments. Experimental distributions usually exhibit a vanishing tail of (very) long chains so that dilution and chain-length effects may then strongly compete with each other. To get a detailed insight in the competitive adsorption thermodynamics, numerical investigations are presumably required. However, at the mean-field level, a crude estimate may be obtained by neglecting chain end effects and thereby logarithmic factors (ground-state approximation). This assumption certainly overestimates the contribution of the small chains, but is a convenient starting point to gain a first idea. Let us further assume that the polydispersity distribution is narrow. A narrow distribution results, for instance, from anionic polymerization and can be mimicked by a Gaussian distribution with mean $\langle N\rangle$ and standard deviation $\sigma = \langle N\rangle(\mathcal{P}-1)^{1/2}$, where $\mathcal{P} = \langle N^2\rangle / \langle N\rangle^2$ denotes the polydispersity. If this (weakly) polydisperse sample is exposed to an attractive wall one expects that the average chain length of the adsorbed chains, $\langle N\rangle_a$, is larger than the bulk value, whereas σ essentially stays the same. Roughly, one finds $\langle N\rangle_a \approx \langle N\rangle(1+(\mathcal{P}-1)\ln[1/\phi^0 b^2])$, where ϕ^0 is the total monomer concentration in the bulk. This result also holds for the often used Poisson distribution. On the other hand, for highly polydisperse samples, as obtained by radical polymerization, for instance, the adsorption is dominated by the largest chain lengths of the distribution. Certainly, these predictions are fairly rough, since the experimental sample contains many short chains whose weight in the layer is overestimated by the presented arguments. However, these examples suggest that a very narrow, but still realistic distribution behaves as a monodisperse sample with a slightly higher average length of the adsorbed chains, at least at moderate dilutions.

In the present work the two polymer species differ only in length. No disparity in interaction energy between (parts of) the chains and the wall is considered. Those enthalpic effects can, however, be important in practice. For polymers of comparable length one expects that the species, which interacts more strongly with the surface, adsorbs preferentially [1]. That a higher interaction energy can, to some extent, even outweigh a difference in chain length was pointed out by a comparative infrared spectroscopy study of deuteriopolystyrene and protiopolystyrene [18]. As long as the length of protiosample did not considerably exceed that of the deuterated polymer the stronger interaction of deuteriopolystyrene with the silicon oxide surface favored its adsorption. This behavior could be reversed if protiopolystyrene carried a highly attractive carboxylic end group. Then the chain length of the deuteriospecies had to be larger by a factor of about 80 to significantly suppress the preferential adsorption of protiopolystyrene [18]. Those and comparable (i.e., block copolymers with blocks of different adsorption ability, etc.) energetic effects can be incorporated in our theoretical framework and are therefore prospective topics of future work.

Another interesting topic is the formation of the equilibrium layer. Since the small chains move faster than the large ones, one expects them to be adsorbed first at the wall. However, in the (very) long time limit they have to be replaced by the large chains. Theoretical studies on monodisperse layers [20] as well as experiments [21] indicate that this replacement is a rather slow process. How the replacement occurs and which dynamic properties determine the layer formation is what we want to investigate next.

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APPENDIX: SOLUTION OF EQ. (2.45)

If the radius of gyration of the short chains is smaller than z^*, the potential is given by $U(z) = 2/z^2$ [see Eq. (2.44)]. With the help of the Laplace transform,

$$\tilde{\mathcal{Z}}_2(E,z) = \int_0^\infty dn\, \mathcal{Z}_2(n,z) \exp[-En],$$

Eq. (2.45) takes the following form:

$$\frac{\partial^2 \tilde{\mathcal{Z}}_2}{\partial z^2} - \left[\frac{2}{z^2} + E\right] \tilde{\mathcal{Z}}_2 = -1, \tag{A1}$$

where the boundary condition $\mathcal{Z}_2(0,z) = 1$ was used. After Laplace transformation the other boundary conditions give

$$\left.\frac{\partial \tilde{\mathcal{Z}}_2(E,z)}{\partial z}\right|_b = -\frac{1}{b} \tilde{\mathcal{Z}}_2(E,b), \tag{A2}$$

$$\lim_{z\to b} \tilde{\mathcal{Z}}_{\mathrm{f},2}(E,z) = 0, \tag{A3}$$

and

$$\lim_{z\to\infty} \tilde{\mathcal{Z}}_2(E,z) = \lim_{z\to\infty} \tilde{\mathcal{Z}}_{\mathrm{f},2}(E,z) = \frac{1}{E}. \tag{A4}$$

The boundary conditions (A2) and (A3) are evaluated at $z=b$ instead of at $z=0$ because the form of the potential that we use diverges as $z\to 0$. Since Eq. (A1) is invariant under the transformation $z \to z+b$, this procedure is legitimate and may be reversed by replacing z with $z+b$ in the final results.

In order to solve Eq. (A1) we first determine the general solution of the homogeneous equation

$$\frac{\partial^2 \widetilde{\mathcal{Z}}^h_2}{\partial z^2}-\left[\frac{2}{z^2}+E\right]\widetilde{\mathcal{Z}}^h_2=0.$$

Inserting the ansatz

$$\widetilde{\mathcal{Z}}^h_{2,\pm}(E,z)=\varphi_\pm(E,z)\exp[\pm Ez] \quad \text{and} \quad \varphi_\pm(E,z)=\sum_{k=0}^{\infty} a_k^\pm \frac{1}{z^k} \tag{A5}$$

yields

$$\widetilde{\mathcal{Z}}^h_2(E,z)=A_+\left[1-\frac{1}{\sqrt{E}z}\right]\exp[\sqrt{E}z]+A_-\left[1+\frac{1}{\sqrt{E}z}\right]\times\exp[-\sqrt{E}z], \tag{A6}$$

where $A_\pm$ are integration constants. A specific solution of the inhomogeneous equation is obtained by the method of the variation of constants

$$\begin{aligned}\widetilde{\mathcal{Z}}^i_2(E,z)=&\frac{1}{E}+\frac{1}{2E}[-\mathrm{Ei}(-\sqrt{E}z)+\mathrm{Ei}(-\sqrt{E})\\&-\exp(-\sqrt{E})]\left[1-\frac{1}{\sqrt{E}z}\right]\exp[\sqrt{E}z]\\&+\frac{1}{2E}[-\mathrm{Ei}(\sqrt{E}z)+\mathrm{Ei}(\sqrt{E})-\exp(\sqrt{E})]\\&\times\left[1+\frac{1}{\sqrt{E}z}\right]\exp[-\sqrt{E}z],\end{aligned} \tag{A7}$$

where $\mathrm{Ei}(x)$ denotes the exponential integral function [17]. The general solution of Eq. (A1) is therefore

$$\begin{aligned}\widetilde{\mathcal{Z}}_2(E,z)=&\frac{1}{E}+\frac{1}{2E}[2EA_+-\mathrm{Ei}(-\sqrt{E}z)+\mathrm{Ei}(-\sqrt{E})\\&-\exp(-\sqrt{E})]\left[1-\frac{1}{\sqrt{E}z}\right]\exp[\sqrt{E}z]\\&+\frac{1}{2E}[2EA_--\mathrm{Ei}(\sqrt{E}z)+\mathrm{Ei}(\sqrt{E})-\exp(\sqrt{E})]\\&\times\left[1+\frac{1}{\sqrt{E}z}\right]\exp[-\sqrt{E}z].\end{aligned} \tag{A8}$$

The boundary condition (A4) fixes the integration constant A_+ for both the total and the free-chain partition function to

$$A_+=A_{\mathrm{f},+}=\frac{1}{2E}[\exp(-\sqrt{E})-\mathrm{Ei}(-\sqrt{E})] \quad , \tag{A9}$$

whereas Eq. (A2) yields for A_- of the total partition function

$$\begin{aligned}A_-=&\frac{1}{2E}[\exp(\sqrt{E})-\mathrm{Ei}(\sqrt{E})+\mathrm{Ei}(\sqrt{E}b)\\&-\mathrm{Ei}(-\sqrt{E}b)\exp(2\sqrt{E}b)],\end{aligned} \tag{A10}$$

and Eq. (A3) for the free-chain partition function

$$\begin{aligned}A_{\mathrm{f},-}=\frac{1}{2E}\Bigg[&\exp(\sqrt{E})-\mathrm{Ei}(\sqrt{E})+\mathrm{Ei}(\sqrt{E}b)\\&-\frac{2\sqrt{E}b}{1+\sqrt{E}b}\exp(\sqrt{E}b)\\&-\frac{1-\sqrt{E}b}{1+\sqrt{E}b}\mathrm{Ei}(-\sqrt{E}b)\exp(2\sqrt{E}b)\Bigg].\end{aligned} \tag{A11}$$

Replacing z with $z+b$, as mentioned before, and using Eq. (2.3) one obtains the partition function of the adsorbed chains

$$\begin{aligned}\widetilde{\mathcal{Z}}_{\mathrm{a},2}(E,z)&=\widetilde{\mathcal{Z}}_2(E,z)-\widetilde{\mathcal{Z}}_{\mathrm{f},2}(E,z)\\&=\frac{b}{z+b}\,\frac{1+\sqrt{E}(z+b)}{E(1+\sqrt{E}b)}\\&\quad\times\exp(-\sqrt{E}z)[1-\mathrm{Ei}(-\sqrt{E}b)\exp(\sqrt{E}b)].\end{aligned} \tag{A12}$$

In a similar fashion one can also calculate the total, the free-chain, and the adsorbed-chain partition function if the radius of gyration of the short chains lies between z^* and λ. Then the potential is $U(z)=20/z^2$. Adding the two homogeneous solutions,

$$\widetilde{\mathcal{Z}}^h_{2,\pm}(E,z)=\left[1\mp\frac{10}{E^{1/2}z}+\frac{45}{Ez^2}\mp\frac{105}{E^{3/2}z^3}+\frac{105}{E^2z^4}\right]\times\exp[\pm\sqrt{E}z], \tag{A13}$$

to the special inhomogeneous solution one obtains for the total partition function

$$\begin{aligned}\widetilde{\mathcal{Z}}_2(E,z)=&\frac{1}{E}-\frac{20}{E^2z^2}+\frac{280}{E^3z^4}+\Bigg[A_+-\frac{1}{2E}\exp[-\sqrt{E}]\\&\times\left(1+\frac{10}{E^{1/2}}+\frac{35}{E}+\frac{35}{E^{3/2}}\right)\Bigg]\widetilde{\mathcal{Z}}^h_{2,+}(E,z)\\&+\Bigg[A_--\frac{1}{2E}\exp[\sqrt{E}]\bigg(1-\frac{10}{E^{1/2}}\\&+\frac{35}{E}-\frac{35}{E^{3/2}}\bigg)\Bigg]\widetilde{\mathcal{Z}}^h_{2,-}(E,z).\end{aligned} \tag{A14}$$

Due to the boundary condition (A4) A_+ has to equal the second term in the bracket so that

$$\begin{aligned}\widetilde{\mathcal{Z}}_2(E,z)=&\frac{1}{E}-\frac{20}{E^2z^2}+\frac{280}{E^3z^4}+\Bigg[A_--\frac{1}{2E}\exp[\sqrt{E}]\\&\times\left(1-\frac{10}{E^{1/2}}+\frac{35}{E}-\frac{35}{E^{3/2}}\right)\Bigg]\widetilde{\mathcal{Z}}^h_{2,-},\end{aligned} \tag{A15}$$

from which one obtains the partition function of the adsorbed chains by

$$\widetilde{\mathcal{Z}}_{\mathrm{a},2}(E,z)=\widetilde{\mathcal{Z}}_2(E,z)-\widetilde{\mathcal{Z}}_{\mathrm{f},2}(E,z)=A_{\mathrm{a},-}\widetilde{\mathcal{Z}}^h_{2,-}(E,z). \tag{A16}$$

The integration constant $A_{\mathrm{a},-}$ is determined in Sec. II B 2.

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