Adsorption of multiblock copolymers at interfaces between selective solvents: Single-chain properties

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We consider the configuration properties of a periodic multiblock copolymer made of a regular alternating succession of two monomer species A and B near interfaces between two weakly selective solvents α and β. Both solvents are assumed to be good, but their quality is slightly different for both monomer species: Solvent α is better for A than for B, and vice versa. We map the problem into a corresponding homopolymer adsorption problem by considering the individual AB-diblock units as effective segments of a coarse-grained chain. The renormalized segments have an effective interaction with the solvent-solvent interface. This is calculated to second order in a perturbation expansion. We show that attraction of a single diblock by the interface is a second-order effect. In the symmetric case the first-order contribution vanishes and the interface is always attractive. The strength of the effective attraction scales as $(\chi n)^2$, where χ is the selectivity strength and n the length of an AB unit. When the interface potential is not symmetric with respect to the block species, a first-order repulsive contribution appears. As a result we predict a discontinuous desorption transition for that case, controlled by the asymmetry. In marked difference to the usual adsorption problem, the largest stable adsorption blob is of finite size.

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I. INTRODUCTION

Copolymers consisting of two different monomer species A and B are currently one of the most intensively studied topics of polymer science. Roughly one has to distinguish between random and periodic copolymers in respect to the distribution of the A and B species along the chain. This work is restricted to periodic multiblock copolymers comprising an alternating succession of A and B blocks with lengths n_A and n_B, respectively. It is possible to consider such copolymers as homopolymers where each "monomer" is an AB diblock.

Much theoretical and experimental work has dealt recently with the behavior of copolymers in selective solvents that are poor for one monomer species and good for another. In order to fix the notation we denote the α solvent, which is better for A and poorer for B. In the opposite case we call it a β solvent.

This paper is concerned with the behavior of ideal periodic copolymers near the interface between an α and a β solvent [1]. When the polymer chain is at the interface both A and B blocks can be in their better solvent [Fig. 1(a)]. Hence, the free energy of the chain is lowered and the chain is attracted by the interface. This is of considerable technical importance since copolymers adsorbed in that way modify the solvent-solvent interface tension.

From the conceptual point of view it is useful to distinguish between two cases: strong and weak interface selectivity.

The interface is strongly selective when both monomer species experience a strong repulsion (compared to $k_B T$) by crossing over from the preferred to the other solvent. Hence, the A blocks are only in the α solvent and the B blocks in the β solvent. As a consequence each AB junction sticks to the interface [Fig. 1(a)]. Dragging it away from it implies an increase of the free energy by more than $k_B T$. So each block is strongly attached to the interface at both ends. The adsorbed chain is located within the size of a single block in the direction perpendicular to the interface [3] $W_{A,B} \sim n_{A,B}^{1/2}$.

In the following we will focus on the opposite case of weak interface selectivity. This means that the two solvents are good for both species but there is a weak repulsion if an $A(B)$ monomer crosses the interface from the $\alpha(\beta)$ into the $\beta(\alpha)$ solvent.

In this case there is a competition between the free-energy gain caused by the orientation of each AB unit at the interface and its conformational free energy. As a result the individual diblocks are only weakly oriented by the interface selectivity though their free energy is lowered compared with the bulk. Hence, in contrast to the case of strong selectivity a single AB unit itself is attracted but not adsorbed.

However, the multiblock copolymer as a whole may adsorb at the interface due to the cooperative effect of the many diblocks it is made of, but the extension of an adsorbed chain in the direction perpendicular to the interface is much larger than the size of a single diblock [Fig. 1(b)].

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Hence two questions arise. First, what is the crossover chain length; the characteristic chain length necessary for adsorption at the interface? Second, what is the width W of the adsorbed polymer chain in the direction perpendicular to the interface well above the adsorption crossover?

In the limit of weak selectivity all relevant distances in the problem are much larger than a diblock size R. This suggests that we may consider the AB units as new statistical segments of a coarse-grained chain, having an effective interface interaction. We will calculate this effective interaction within a perturbation expansion.

The parameters necessary for the description of the adsorption behavior are both block lengths and chemical potentials of the solvents. As we will see, there is a *symmetry line* where the chain is always attracted. The simplest realization of this symmetry is what we call the fully symmetric case. Here both block lengths are equal, $n_A = n_B$, and the differences of the solvent qualities (selectivity) for both monomer species by crossing the interface are also equal.

However, if this symmetry condition is violated the interface acts like a combination of a potential step and an attractive part. Competition between both parts gives rise to a phase diagram comprising an adsorbable region and a region where adsorption is not possible even for infinite chain lengths.

As we will see, the adsorbable region around the symmetry line is very small. Hence, the interface is very selective with respect to different copolymer architectures: only those copolymers that are very close to the symmetry condition are adsorbed.

The paper is organized as follows: In Sec. II we define the coarse-graining procedure and develop the perturbation expansion for a single diblock. In Sec. III we present the results for the fully symmetric case for the potential as well as for the block lengths. The general asymmetric case is considered in Sec. IV. We conclude the paper with a discussion of the results in Sec. V.

To avoid repetition we take $k_B T$ as the unit of the energy.

II. RENORMALIZATION PROCEDURE AND PERTURBATION EXPANSION

The interaction potential of monomer s at distance z in the direction perpendicular to the interface will be denoted by $V(z, s)$. Since we have only two monomer species A and B there are only two different potentials $V_A(z)$ and $V_B(z)$.

The left part of Fig. 2(a) shows a possible realization. Since the interaction of one monomer species with the corresponding potential is completely independent of the
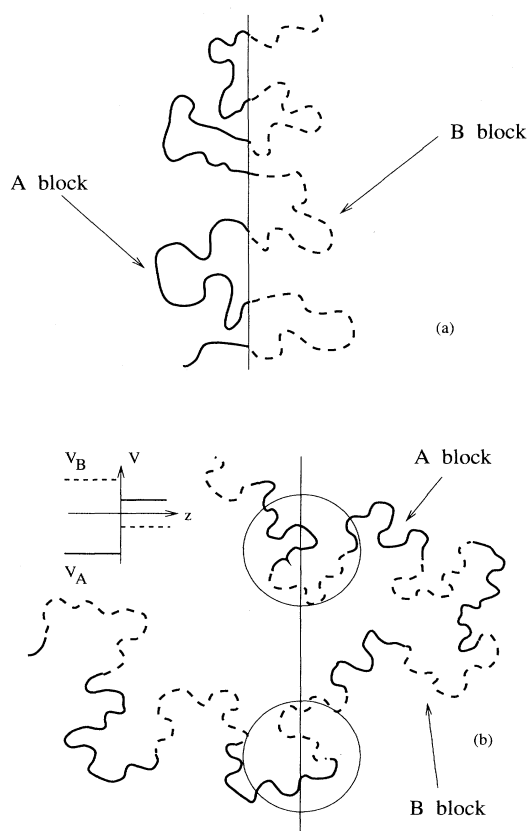

FIG. 1. (a) Multiblock copolymer at a strongly selective interface. All junction points between different blocks stick at the interface. Each block configures freely within its preferred half space. (b) Multiblock copolymer near a weakly selective interface. Only parts of the chain that actually cross the interface (surrounded by circles) will be weakly oriented and can lower the free energy. Most of the blocks are completely on one solvent side. Every monomer feels an interaction potential near the interface sketched in the upper left corner. It differs between the A and B species so that the left side is preferred by the A blocks and the right side by the B blocks.
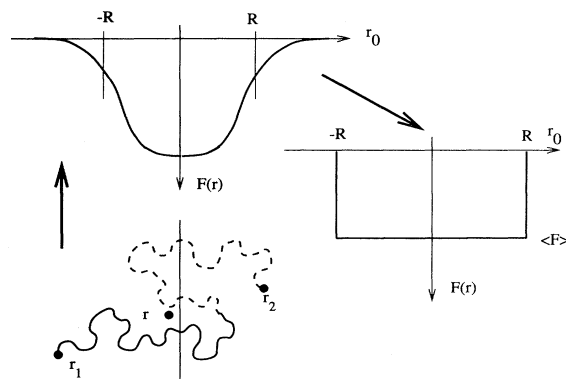

FIG. 2. (a) A possible realization of the selectivity potential in the general case. Since only the potential differences matter for both species independently, it is possible to gauge them as sketched in the right-hand side. The individual potential differences are denoted by χ_A and χ_B, respectively. For the case of a fully symmetric potential (b) a different gauge is more convenient. Going over from one species to the other the potential is simply mirrored. This allows for the separation of arclength and spatial dependencies.

other we can gauge both potentials in an arbitrary way. One can understand this, for instance, by considering the diffusion dynamics of the monomers. As long as a given monomer does not cross the interface it moves in a constant potential and the motion is unaffected by that potential. If it does cross the interface only the *difference* or the potential step matters. This is true for both species independently. Hence, only the differences $[\Delta V_A(z), \Delta V_B(z)]$ are physically relevant quantities. We will gauge the individual potentials for the general asymmetric case as sketched in the right part of Fig. 2(a). The corresponding quantitative expressions are

$$V_A(z) = \begin{cases} \chi_A, & z < 0 \\ 0, & z \geq 0, \end{cases}$$

$$V_B(z) = \begin{cases} 0, & z \leq 0 \\ \chi_B, & z > 0. \end{cases} \tag{1}$$

However, if the selectivity potential is symmetric with respect to the monomer species we will use the gauge given in Fig. 2(b). This gives us the possibility to separate the interaction potential in the following way:

$$V(z,t) = U(z)b(t). \tag{2}$$

$U(z)$ is the value of the interaction of one block species (A), at the distance r perpendicular to the interface. $b(t)$ characterizes the arrangement of A and B monomers along the chain. We will call $b(t)$ the *block structure function*. For the symmetric gauge [Fig. 2(b)], going from one monomer species to the other means simply switching the *sign* of the function U. Hence $b(t)$ has the form of Heaviside's function:

$$b(t) = \begin{cases} 1, & 0 < t \leq n_A \\ -1, & n_A < t < n, \end{cases} \tag{3}$$

where n_A is the length of an A block and $n_B = n - n_A$ the corresponding length of the B block.

There exists an interesting analogy to a corresponding quantum mechanical problem: Firstly, $b(t)$ is a simple periodic function for the multiblock copolymer chain as a whole in the case $n_A = n_B$. On the other hand it is well known that the configuration properties of a polymer chain can be described by a Schrödinger-like differential equation with the proper coupling of an external potential. Hence the differential equation describing the Green function of a polymer chain with a potential given by Eq. (2) is very reminiscent of the propagation of a Schrödinger particle in a *time-fluctuating* field. We discuss this analogy in detail in Sec. III B and Appendix A.

In Figs. 2(a) and 2(b) we have considered sharp interface potentials that may be approximated as step functions. More realistic would be a smooth variation of the following form:

$$V_{A,B}(z) = \chi_{A,B} \tanh(z/w_{A,B}) \ . \tag{4}$$

If the characteristic width of the potential w is much smaller than the extension of a single diblock the step function approach is sufficient. In the opposite case w be-

comes a characteristic parameter controlling the diblock-interface interaction too. For the general asymmetric case we will only consider the step-function approach in this work.

We consider ideal chains and separable interaction potentials as a function of z only. Hence, it is sufficient to treat the direction perpendicular to the interface only. There is no coupling between the different spatial directions and the behavior parallel to the interface is simply ideal.

As mentioned in the Introduction, the copolymer chain can be considered as a homopolymer made of a succession of f head-tail linked identical diblocks. This suggests introducing a renormalization step averaging out all details within the scale of a single diblock. This procedure can be justified mathematically as follows.

First of all, the partition function is an integral over all monomer positions of the chain weighted with the appropriate potentials for the next-neighbor bonds along the chain and external potentials. The way these integrations are carried out has to be arbitrary.

We start by integrating out all internal monomer positions of the individual diblocks first. Only the junction points that link the diblocks to each other should be left over. We assume for simplicity that they are neutral with respect to the selective potential.

The internal integration gives for each diblock a contribution Z that depends on its initial and final positions. We can write it in the form $Z = e^{-F_{\text{Gauss}} - \Delta F}$. F_{Gauss} is a corresponding harmonic contribution for the coarse-grained chain [see Eq. (5)]. It can be extracted since it is known that the renormalized chain possesses a simple chain connectivity. Hence we have reproduced a partition function for a coarse-grained polymer chain that is now a homopolymer and each monomer has the same effective interaction ΔF.

So far no approximations are made and the renormalized partition function is exactly the same as the original one. However, we are not interested in the behavior of the chain on length scales smaller than the size of a diblock. Hence, the effective diblock-interface interaction can be simplified as a function of the central position of a given diblock only: $r = \frac{z(n)+z(0)}{2}$ [$z(n)$ and $z(0)$ are the final and the initial positions of the diblock, respectively]. This neglects fluctuations on scales of the order R. Figure 3 illustrates the described steps of the procedure. The free energy for each configuration $\{r_i\}$ of the renormalized chain takes the form

$$F_{\text{chain}}(\{r_i\}) = \frac{1}{2R^2} \sum_i^{f-1} (r_{i+1} - r_i)^2 + \Delta F(r_i) \ , \tag{5}$$

where R is the averaged end to end distance of a diblock [2]. Hence the calculation of the effective interface interaction of a single diblock $\Delta F(r)$ is the basic step in our approach. We consider now this problem in more detail.

A given diblock will have a favored solvent side if it is far away from the interface, i.e., completely in one solvent. This is generally so when the symmetry equation

$$n_A \chi_A = n_B \chi_B \tag{6}$$

is violated. Let us denote the free energy in the preferred solvent side by $F_0 = \min(n_A\chi_A, n_B\chi_B)$. Since a constant free energy or chemical potential does not matter, only the difference $\Delta F(r) = F(r) - F_0$ is relevant.

Two qualitatively different effects occur if the diblock approaches the interface from the favored side. First, the free energy increases since parts of the diblock are dissolved in the other solvent. On the other hand, the diblock will be polarized due to interface selectivity, which lowers its free energy; see Fig. 5. We will demonstrate that the competition of these two effects governs the adsorption of the whole copolymer chain at the interface.

In the symmetric case when the average solvent quality is equal in both solvents only the polarization contribution is present and the copolymer can be adsorbed.

We consider now the calculation of the effective free energy $\Delta F(r)$ of a single diblock near the interface. Since the selectivity potential is weak, a perturbation expansion with respect to $V(z, s)$ is appropriate. The free-energy expansion $F(r)$ up to second order takes the general form

$$F(r) = \langle V \rangle_0(r) - \tfrac{1}{2}[\langle V^2 \rangle_0(r) - \langle V \rangle_0^2(r)] \pm \cdots \ . \quad (7)$$

The two contributions can be written in terms of Green functions of the unperturbed ideal chain,

$$G(x, s) = \left(\frac{1}{2\pi|s|}\right)^{1/2} \exp\left(-\frac{x^2}{2|s|}\right) \quad (8)$$

as follows:

$$\langle V \rangle_0 = 2 \int_0^n ds \int_{-\infty}^{\infty} dy\, V(y, s) G(2y - 2r, n) \quad (9)$$

and

$$\langle V^2 \rangle_0 = 4 \int_0^n dt \int_0^t ds \int_{-\infty}^{\infty} dx\, dy\, G(x - y, t - s) G(x + y - 2r, n - t + s) V(x, s) V(y, t) \ . \quad (10)$$

The factor 2 in Eq. (9) arises for the proper normalization by going over to the center coordinate. For Eq. (10) the arclength ordering gives an additional factor of 2.

We end this section with a few general remarks about the potential used. It is assumed that both solvents are of slightly different quality for both species but with both being good. In the case when one solvent quality is close to the Θ point, the configuration statistics of the blocks is changed by crossing the interface. In an extreme case both block species could be in a swollen configuration in the favored solvent and in a collapsed configuration in the other solvent. However, the last scenario cannot be described within a bare perturbation expansion. The case where both solvents qualities are around the Θ point for both species would allow for a weak potential difference but will not be considered here.

III. SYMMETRIC CASE

We start with a discussion of a symmetric selectivity potential using Eq. (2). More precisely $U(z)$ interpolates between $-\chi$ for $z \to -\infty$ and $+\chi$ for $z \to +\infty$. For simplicity we assume $U(z) = -U(-z)$. The diblock architecture is also considered to be symmetric: $n_A = n_B$.

Since the potential and the block chemical structure are assumed to be symmetric, $F(r) = \Delta F(r)$ vanishes if r is much larger than the radius of gyration R of the diblock. On the other hand, if the width w [see Eq. (4)] is much larger than R, $F(r)$ is nonzero for all positions within a distance w. The first-order contribution according to Eq. (9) takes the form

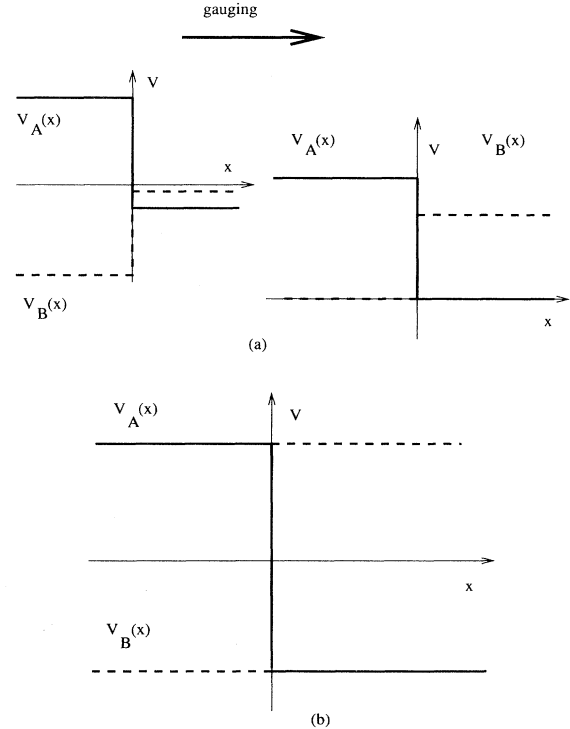$$\langle V \rangle_0 = 2 \int_0^n b(t) dt \int dx\, G(2x - 2r, n) U(x). \quad (11)$$

FIG. 3. Renormalization procedure. The chain is considered as a succession of head-tail linked diblocks. At the first step the junction point denoted here as a bullet is keep fixed while the averaging over the rest of the monomers is carried out. Before the coarse-graining procedure, the potential $V(r(s))$ depends on the actual position r of every monomer s. After averaging out the middle monomers the effective potential ΔF depends only on the set of fixed points $\{z_k\}$. It is convenient to go over to an alternative set of coordinates $\{r_k\}$ which corresponds to the center positions of the renormalized segments. This results in the function $\Delta F(r_k)$.

If $n_A = n_B$ or more precisely $\int_0^n b(t) = 0$, there is no contribution from $\langle V \rangle_0$.

We now consider the second-order term in Eq. (7) given by Eq. (10). Using Eq. (2) we have

$$\langle V^2 \rangle_0 = 4 \int_0^n dt \int_0^t ds\, b(s)b(t) \int_{-\infty}^{\infty} dx\,dy\, G(x-y, t-s)G(x+y-2r, n-(t-s))U(x)U(y). \tag{12}$$

It is now possible to get all the n, u, and w dependences without really doing the remaining integrals. Let us introduce scaled variables in the following way: All arclength parameters should be given in units of n and all spatial scales in units of $\sqrt{n}$. Equation (8) gives us the corresponding scaling for G. $U(x)$ can be written as $\chi I(x, w)$ where I interpolates between -1 and 1. Quite generally we can assume $I(x, w) = I(x/w)$. As a result the integral of the scaled variables depends only on $w/\sqrt{n}$ and $r/\sqrt{n}$. Using Eq. (8) the general form of the above expression is

$$F(r) \simeq -\frac{1}{2}\langle V^2 \rangle_0 = -\chi^2 n^2 \kappa\left(\frac{w}{\sqrt{n}}, \frac{r}{\sqrt{n}}\right), \tag{13}$$

where κ is the result of the integration. The effective potential for a single diblock now has a form that is easily treatable for the following special cases.

A. Sharp interface potential

For the case $w \ll \sqrt{n}$, $I(x)$ can be approached by a steplike function. This means that there is no scaling for $w/\sqrt{n}$. The only dependence left in κ comes from r.

The renormalization step provides a smooth potential $F(r)$, which basically extends from $-R$ to R; see Fig. 4. However, we are not interested in the behavior on scales smaller than R. So it will be sufficient to average the effective potential $F(r)$ over the interval $(-R, R)$ and replace it by a boxlike shape. This is also sketched in Fig. 4. Hence, we introduce an average effective potential of the diblocks $\overline{F}(r)$:

$$\overline{F}(r) = \begin{cases} 0, & r \geq R \\ \langle F \rangle, & -R < r < R \\ 0, & r \leq -R, \end{cases} \tag{14}$$

where $\langle F \rangle$ is

$$\langle F \rangle = -\chi^2 n^2 \frac{1}{2R}\int_{-R}^{R} dr\,\kappa(0, r/\sqrt{n}) = -\chi^2 n^2 \kappa_0 \ . \tag{15}$$

κ_0 is a positive numerical positive constant independent of the size of the diblock and of the strength of the selectivity. It may be computed numerically.

Note that $F_{\min}$, the minimum of $F(r)$, scales in the same way: $\langle F \rangle \sim F_{\min} = F(0)$. In Sec. IV we consider the minimum value $F_{\min}$ instead of $\langle F \rangle$ because it is easier to handle in the asymmetric case. If we are not interested in the precise values of the constant prefactors it makes no difference whether $\langle F \rangle$ or $F_{\min}$ is used.

We obtained an explicit expression for the effective attraction of a single diblock near a selective interface. The interaction F is short ranged if R is considered as the smallest scale of interest. Its value scales with the square of the product of block length n and the selectivity χ. The multiblock copolymer chain may be considered as a homopolymer weakly attracted by the interface with strength $\langle F \rangle$.

B. Smooth interface potential

For $w \gg R$ an additional scaling arises from $w/\sqrt{n}$ in the integral κ. Using Eq. (4) for the selectivity potential three different regions may be distinguished. For $|z/w|$
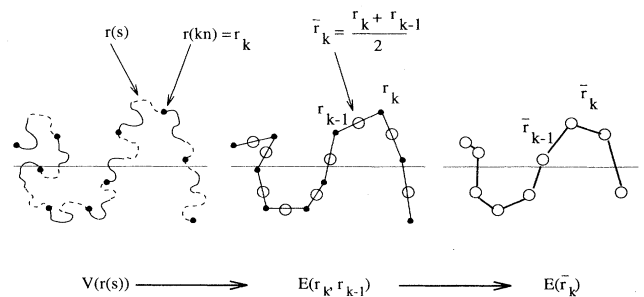

FIG. 4. Effective interface interaction for a single diblock. Fixing the center of mass r the average interaction free energy F has a shape sketched in the upper right part. Basically it is extending from $-R$ to R. Since the renormalization procedure "washes out" the details for scales smaller than R along the chain it makes sense to average the effective interaction on this scale. The result is a boxlike attraction potential $\overline{F}$ given in the right part of the figure.

larger than unity the potential reaches the asymptotic values $-\chi$ or χ. Hence the effective interaction potential goes to zero as expected. w gives its range. In the case where $|z/w|$ is much smaller than unity it can be approximated by a linear function. We will call this region the gradient region. Finally, there remains a crossover region in between both. We will calculate the effective potential for the gradient region exactly. This can be done in principle with the whole series expansion of the tanh

function. However, because this gives no more insight into the physics behind it, we propose an interpolation function capable of describing the crossover to the sharp interface as well.

In the gradient region we have $I(\frac{z}{\sqrt{n}}/\frac{w}{\sqrt{n}}) = \frac{z}{\sqrt{n}}/\frac{w}{\sqrt{n}}$. However, in this case the remaining integrals are solvable. So we can obtain the numerical constant as well. In the present case $F(r)$ takes the form

$$F(r) = -\chi^2 n^3 w^{-2} 2 \int_0^1 \int_0^1 dsdt \; b(s)b(t) \int\int dxdy \; G(x-y,t-s)G(x+y-2r/\sqrt{n},1-(t-s))xy. \qquad (16)$$

The x,y integrations are now standard Gaussian integrals after decoupling them by transforming the integration variables into $\overline{x} = x - y$ and $\overline{y} = 1/2(x+y)$. The result is

$$F(r) = -\chi^2 n^3 w^{-2}/24 \;, \qquad (17)$$

independent of r.

The averaging over R is not necessary since the effective potential is constant in the gradient region. Moreover, the approach is the exact result since the interaction potential $V(z(s))$ is linear in $z(s)$.

The crossover region provides higher-order terms in n/w^2 than the result in the above equation. These will also depend on r. Since we assume that $n/w^2 \ll 1$ the correction from the crossover region can be neglected. We can assume a constant effective attraction of the diblocks given by the above equation in the interval $(-w,w)$.

However, it is possible to give a convenient interpolation function from the smooth to the sharp interface behavior. Comparing Eqs. (15) and (17) the following function is suggested:

$$\langle F \rangle = -\chi^2 n^2 \left(\frac{\sqrt{\kappa_0} R}{\sqrt{24 \kappa_0} w + R} \right)^2 \;. \qquad (18)$$

We show in Appendix B that the scaling approach naturally yields an expression like this.

It is interesting to compare these results with those by Cook, Shakland, and Wells (CSW) [4]. These authors considered the possible localization of an electron in a time-periodic external field. They give an explanation for the so-called Pauls traps. It is well known that the propagation of a Schrödinger particle in an external field is described by an equation very similar to that describing the configuration of polymer chain in a corresponding field.

Thus the trapping of a Schrödinger particle in a time-fluctuating field is very reminiscent of the attraction of a multiblock copolymer chain in a symmetric selective potential; both systems are described by the same Hamiltonian. The time variable in the quantum-mechanical problem corresponds to the arclength parameter of the

polymer chain. The eigenvalue problem is exactly the same. In Appendix A this method is reconsidered for the polymer case.

The basic idea is to separate the Green function for a periodic multiblock copolymer into rapidly oscillating and slowly varying parts. The fast part oscillates with a period of the diblock length and will be dropped. The differential equation for the slow part is again a Schrödinger equation with an effective Hamiltonian. The leading contribution after averaging over the period is an attractive potential independent of arclength. It has the general form

$$U_{\text{eff}} = -n^2 \frac{l^2}{9 \times 32} (\nabla U)^2 \;. \qquad (19)$$

A difference is that the resulting effective equation for the polymer is not coarse grained. That means the above potential is the effective attraction for a monomer rather than for a diblock.

For the smooth interface the CSW method gives the same scaling as the renormalization approach. Coarse graining instead of averaging in the derivation of the above equation would yield an additional factor of n for the effective diblock attraction. However, the above equation gives a numerical constant for the effective attraction much smaller than Eq. (17). An advantage of the CSW method is the easy treatment of attraction potentials like a tanh function.

It has been shown in [4] and [5] that for the sharp selective case this approach breaks down. In this situation the contributions from the other terms of the effective Hamiltonian (see Appendix A) become important too. This yields a more complicated equation than the original one.

We found that in the complete symmetric case (block as well as potential symmetry) the effective attraction of a single diblock by the interface follows simple power laws with respect to the interaction potential and the block length. It is usually possible then to derive the results up to numerical constants using scaling arguments only. In Appendix B we present such a simple scaling approach using a Flory-type argument.

TABLE I. The various adsorption crossover values for both the sharp and the smooth interface potential cases.

	$\langle F \rangle_c$	χ_c	f_c	n_c
$w^2/n \ll 1$	$f^{-1/2}$	$f^{-1/4}n^{-1}$	$\chi^{-4}n^{-4}$	$f^{-1/4}\chi^{-1}$
$w^2/n \gg 1$	$f^{-1/2} \cdot \left(\frac{n}{w^2}\right)^{1/2}$	$f^{-1/4}n^{-1}\left(\frac{n}{w^2}\right)^{-1/4}$	$\chi^{-4}n^{-4}\left(\frac{n}{w^2}\right)^{-1}$	$f^{-1/5}w^{2/5}\chi^{-2/5}$

C. The adsorption crossover

We will now discuss the behavior of the multiblock copolymer chain as a whole in the presence of a weakly selective interface. As shown above this can be mapped into the discussion of a homopolymer consisting of f statistical segments. Each of them is weakly attracted by the interface with a potential $\langle F \rangle$. This is the usual polymer adsorption problem studied intensively in the literature (see, for instance, [7–9]). For the case of a sharp interface the attraction extends only over the range of a statistical segment of length R. An interesting point is that we were naturally led to polymer adsorption at a *penetrable interface*. Hence, our problem brings a nonpathological realization of that problem to our attention [10].

We will treat the adsorption crossover within a scaling approach. In particular we derive the adsorption crossover value $\langle F \rangle_c$ necessary to fix the chain at the interface and the width W of the adsorbed chain for attraction strengths much larger than $\langle F \rangle_c$.

We first assume that $\langle F \rangle$ causes only a weak perturbation of the chain configuration. The chain consisting of f repeat units near the interface will have on the average

$$f_s \sim f w_{\rm eff}/\mathcal{R} \tag{20}$$

repeat units within a penetrable interface of effective width $w_{\rm eff}$. If the interface is sharp its effective width $w_{\rm eff}$ is equal to a single diblock size R, as shown above (Fig. 4). While for the smooth interface $w_{\rm eff}$ corresponds to w. $\mathcal{R}$ is the radius of gyration of the unperturbed copolymer (R is the effective statistical segment length). Hence, the average interaction energy with the interface is $f_s\langle F \rangle$ [6]. If this becomes much larger than $k_B T$ (or unity in our convention) the chain is not only weakly disturbed but is going to stick at the interface. So the localization crossover for a single interface can therefore be defined by

$$|f_s\langle F \rangle_c| \sim 1 . \tag{21}$$

For the case of the sharp interface we obtain from Eq. (20) $f_s \sim f^{1/2}$. The crossover values of the various variables can be calculated using Eqs. (15) and (21). We mark them with an index c. They are listed in the first row in Table I. In the opposite case of smooth interface we have $N_s \sim f^{1/2}w/n^{1/2}$. Taking into account

the corresponding Eq. (17) this yields the results in the second row of Table I.

Hence, we get a phase diagram describing the localization behavior around a single interface. Moreover, the interpolation formula in Eq. (18) or (B5) may be used for $w \sim \sqrt{n}$ but we will not do this explicitly.

We consider now the case when $\langle F \rangle \gg \langle F \rangle_c$. Usually a scaling function can be written down at this point. We will use the corresponding blob approach. Let us assume a part (or blob) of the original chain consists of g adsorption units (diblock units). When g is small enough the interaction with the interface is only a small perturbation. Hence the above argumentation can be completely repeated for g instead of f. If g is of the order f_c given by the fourth column in Table I the blobs will stick at the interface. The adsorption blobs are considered to be just on the verge of being adsorbed. The whole chain can then be considered as a two-dimensional chain of f/g blobs fixed in the interface. Perpendicular to the interface the chain is localized within a width W given by the size of a blob. Using the results of Table I yields

$$
\begin{aligned}
W &\sim \chi^{-2}n^{-3/2}, & w^2/n &\ll 1 \\
W &\sim \chi^{-2}n^{-3/2}\left(\frac{n}{w^2}\right)^{-1/2}, & w^2/n &\gg 1.
\end{aligned}
\tag{22}
$$

IV. THE ASYMMETRIC CASE

The fully symmetric case described above is a very special situation. It requires both a symmetric block architecture and a two symmetric solvents in respect to the block species. In this section we discuss the general case of arbitrary solvent-potential asymmetry and block lengths.

The calculation in the previous section is not general enough to discuss the case of an asymmetric potential. Here the potential does not factorize as in Eq. (2) and hence the block structure function does not decouple from the spatial integrations. As a result we have three scaling parameters. We choose as independent parameters $a = \chi_A n_A$ and $b = \chi_B n_B$ and the block length ratio $p_A = n_A/n$ ($n = n_A + n_B$). The case where p_A is very small or very close to 1 respectively can be considered separately. We will show that there is a finite, not very large, derivation from the block-symmetric case $p_A = 1/2$ then.

We will give a scaling approach for the leading asymmetry effect that is proved by the numerical integration of the result of the perturbation expansion.

A. Perturbation expansion

Using Eqs. (1) and (9) we obtain for the first-order contribution:

$$\langle V \rangle_0 = \frac{1}{2}(a+b) + \frac{1}{2}(b-a)\mathrm{erf}\left(\frac{2r}{\sqrt{2n}}\right) \ . \qquad (23)$$

The error function is defined as usual: $\mathrm{erf}(x) = 2/\sqrt{\pi} \int_0^x e^{-y^2} dy$. As discussed in Sec. II we may subtract the free energy in the favored average solvent state F_0. This can be written as $F_0 = \min(a,b)$. Hence the reduced first-order contribution $\Delta F^{(1)}(r)$ is given by

$$\Delta F^{(1)}(r) = \frac{1}{2}|a-b|\mathrm{erfc}\left(\mathrm{sgn}(b-a)\frac{\sqrt{2}r}{\sqrt{n}}\right) \geq 0 \ . \qquad (24)$$

The complementary error function is defined as $\mathrm{erfc} = 1 - \mathrm{erf}$ and $\mathrm{sgn}(x)$ is the sign of x.

As can be obtained from the above equation there is no localization effect in the first order. $\Delta F^{(1)}(r)$ is always positive. The symmetry point is given by the condition (6): $a = b$ where the first-order contribution vanishes.

In the second order the leading contribution of the perturbed chain configuration is implicitly used, so that the chain will feel the feedback of the interface potential. This leads to a polarization effect of the diblock at the interface. A short derivation of the integral expression used for the numerics is given in Appendix C.

$\langle V^2 \rangle_0$ has three contributions as shown in Appendix C:

$$\langle V^2 \rangle_0 = 4a^2 \frac{1}{p_A^2} I_1(p_A, r) + 4b^2 \frac{1}{(1-p_A)^2} I_2(p_A, r)$$
$$+ 4ab \frac{1}{p_A(1-p_A)} I_3(p_A, r) \ , \qquad (25)$$

where the integrals I_1, I_2, and I_3 are given in Appendix C.

Besides this, we consider the limiting case of very small ratios of the block length, i.e., $p_A \simeq 0$ or $p_A \simeq 1$, respectively, but finite values of a and b. For explicit results see Appendix C.

Before we discuss the numerical results we present a simple argument that leads us to a parameter characterizing the strength of the asymmetry effect in the leading order. However, we will see in Sec. IV C that adsorption is possible only in the case where this asymmetry parameter is small number.

Let us introduce two new parameters instead of a and b:

$$\langle e \rangle = \tfrac{1}{2}(a+b), \qquad (26)$$

$$\Delta e = (b-a) \ , \qquad (27)$$

where $\langle e \rangle$ is the *averaged selectivity* and Δe the *asymmetry of the selectivity* potential.

Using Eqs. (7), (24), and (25) we can write ΔF in the general form:

$$\Delta F = -(\langle \mathbf{e} \rangle + \Delta \mathbf{e})\mathbf{M}(p_A, r)(\langle \mathbf{e} \rangle + \Delta \mathbf{e}) + |\Delta e| P(r). \qquad (28)$$

The vector $\langle \mathbf{e} \rangle$ is defined as $\{\langle e \rangle, \langle e \rangle\}$ and $\Delta \mathbf{e}$ is given by $\{-\Delta e/2, +\Delta e/2\}$. $\mathbf{M}$ is a 2×2 matrix containing the above given integrals as elements. The scalar expression $|\Delta e| P(r)$ is the first-order term given by Eq. (24), hence $P(r)$ is given by $\Delta F^{(1)}(r)/|\Delta e|$. Since $\langle e \rangle$ is by definition a small number the leading contribution is given by

$$\Delta F \simeq -\langle e \rangle^2 M(r, p_A) + \Delta e P(r)$$
$$= -\langle e \rangle^2 \left(M(r, p_A) - \frac{\Delta e}{\langle e \rangle^2} P(r) \right) \ , \qquad (29)$$

where M is defined as the sum over all matrix elements of $\mathbf{M}$. The corrections to that scaling will be of the order $\Delta e/\langle e \rangle$.

One can see that ΔF scales as the square of the average selectivity for vanishing asymmetry. This is qualitatively the same result as in the fully symmetric case; see Eq. (15). However, in the present case it depends also on the block structure because M is a function of p_A. The asymmetry appears only in the scaled form $\Delta e/\langle e \rangle^2$. We define the *asymmetry parameter* as $\Gamma = \Delta e/\langle e \rangle^2$.

Starting from the above approach we will discuss the scaling of the minimum of ΔF, since this is the characteristic parameter for the effective attraction. The equation $\partial \Delta F(r)/\partial r = 0$ is given by

$$\Gamma P'(r_{\min}) = M'(r_{\min}, p_A) \ , \qquad (30)$$

where $r_{\min}$ denotes the minimum value of r. Hence, the minimum delocalization can be written by a scaling function:

$$r_{\min} = h^\pm(\Gamma, p_A) \ . \qquad (31)$$

The upper index $\pm$ denotes the fact that $h^\pm$ is not necessarily symmetric by changing the sign of Γ. For small asymmetry parameter $h^\pm$ may by expanded in series as follows:

$$h^\pm \simeq (p_A - 1/2)^2 h_0^\pm + \Gamma h_1^\pm(p_A) \ . \qquad (32)$$

The numerical results show that in the symmetric case $\Gamma = 0$ the minimum is shifted by a small amount if $p_A \neq 1/2$.

On the other hand, $P(r)$ can be expanded into $P(r) \sim P_1 r$; see Eq. (24). $M(r, p_A)$ can be approached by $m_0(p_A) + m_2^\pm(p_A)r^2$ for small r.

Hence, the minimum of the free energy can be written in the form

$$\Delta F_{\min}(\Gamma) \simeq -\langle e \rangle^2 m_0(p_A) g^\pm(\Gamma)$$
$$= \Delta F_{\min}(0) g^\pm(\Gamma) \ . \qquad (33)$$

From the series expansion of the individual terms one can obtain the approach of $g^\pm$ for small asymmetry pa-

rameters. It takes the form

$$g^{\pm}(\Gamma) = 1 + q_1^{\pm}\Gamma^2 + q_2^{\pm}\Gamma(p_A - 1/2)^2 r_0$$
$$+ q_3(p_A - 1/2)^4 r_0^2 \ . \tag{34}$$

The coefficients q and r_0 are combinations of the expansion coefficients h and m given above. The numerics shows that r_0 is a small number. Hence the derivation to the leading scaling of $\Delta F_{\min}$ are second order in Γ.

B. Numerical results

We will now discuss the numerical results for the interfacial free-energy contribution in the second-order $\Delta F = \Delta F^{(1)} + \Delta F^{(2)}$ to verify the above scaling arguments. Beyond this, some details of the behavior of the solution can be visualized. The limits of the scaling approach as well as the scaling functions can be obtained.

Only the multiple integrals I_1 and I_3 have to be calculated numerically. I_1 and I_2 are of the same type by mirroring the r coordinate. We did this for 81 different r values chosen equidistant between $r/R = -2$ and $r/R = 2$.

Figure 5 shows the comparison between the first- and

FIG. 6. The free-energy function per diblock for different values of Γ plotted against the reduced distance to the interface r/R. The block structure is symmetric and the average selectivity is $\langle e \rangle = 0.1$. The asymmetry parameter Γ takes the values $0, 0.5, 0.75, 1, 2$. For values larger than 1 the minimum is extremely reduced. The first-order contribution dominates.
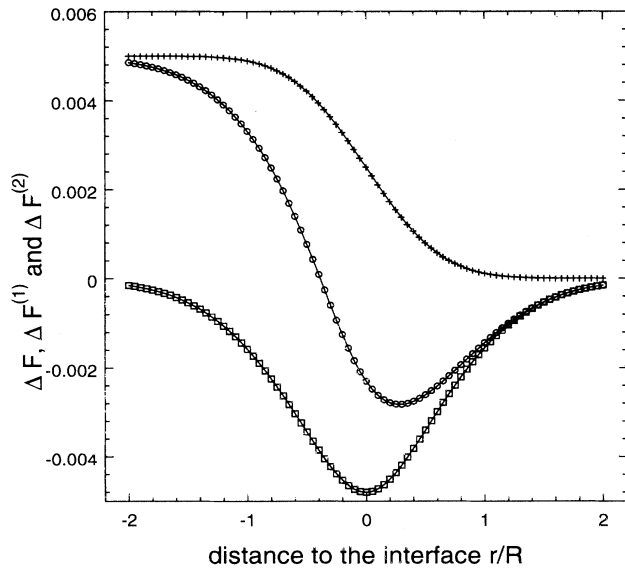

FIG. 5. Plot of the free energy $\Delta F(r/R)$ together with the first- and second-order contribution. The parameters are $\langle e \rangle = 0.1$, $\Delta e = -0.005 \rightarrow \Gamma = -1/2$, and $n_A = n_B$ ($p_A = 1/2$). The favored solvent is on the right-hand side ($a > b$). The first-order contribution (upper curve) is repelling the diblock from the interface. The second-order contribution is attracting (polarization effect). The whole second-order contribution hence shows both features. The minimum is shifted into the favored solvent and is lifted up due to the first-order contribution. For larger distances the nonfavored solvent becomes purely repulsive.
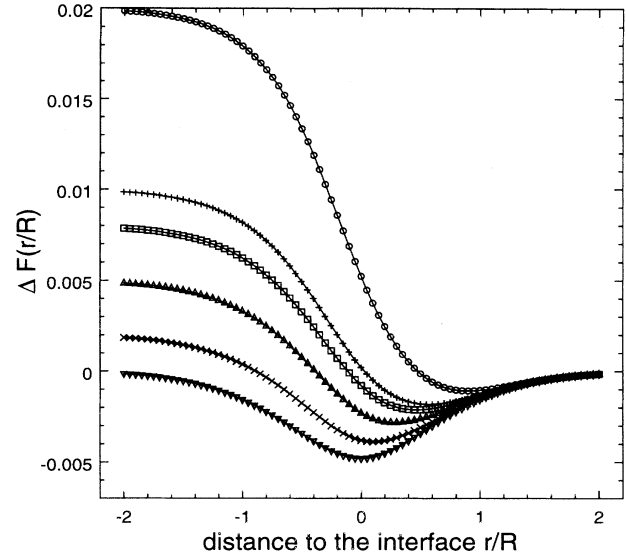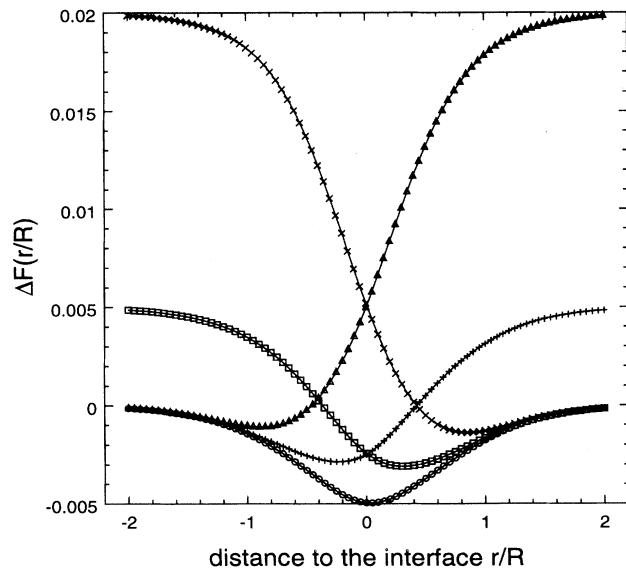

FIG. 7. The free-energy function per diblock as a function of the reduced distance to the interface r/R. The block structure is asymmetric $p_A = 0.8$. The average selectivity is $\langle e \rangle = 0.1$. The asymmetry parameters are chosen as $0, \pm 1/2, \pm 2$. The curves for nonvanishing asymmetry are not mirror symmetric. The shift of the minimum and the depth are different for positive and negative asymmetry parameters, respectively.

the second-order contribution $\Delta F^{(1)}$ and $\Delta F^{(2)}$, respectively, together with the sum, the complete second-order contribution. The parameters for that plot are $p_A = 0.5$, $\langle e \rangle = 0.1$, and $\Delta e = 0.005$. The corresponding asymmetry parameter is $\Gamma = 1/2$. Note that the free-energy change by crossing the interface is already larger than the depth of the minimum.

Figure 6 shows the interfacial free energy for different asymmetry parameters Γ ranging from 0 to -2. Again, a symmetric diblock configuration is chosen, i.e., $p_A = 0.5$.

Note the strong shift of the free-energy minimum into the favored solvent when the asymmetry parameter becomes of the order unity.

In Fig. 7 the situation is shown for $p_A = 0.8$, i.e., nonsymmetric diblocks. The plots are not mirror symmetric with respect to r by changing the sign of the asymmetry. For positive symmetries ($b > a$, left-hand side is preferred) we have a smaller shift of the minimum $r_{\min}$ but a stronger liftup of its value $\Delta F_{\min}$; see also Figs. 8(c) and 9(c).
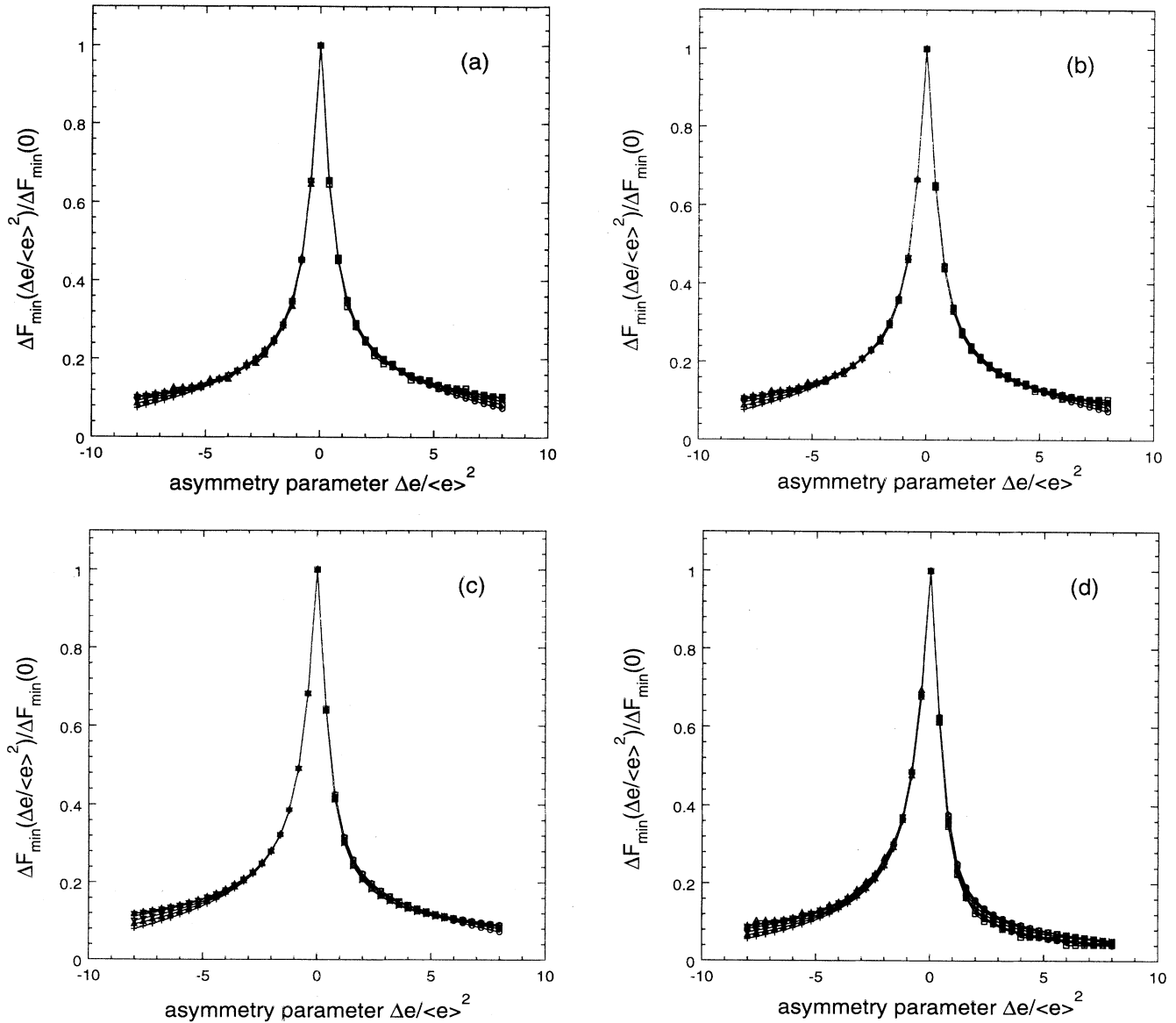

FIG. 8. Reduction of the depth of the free-energy minimum as a function of the asymmetry parameter Γ. Eight different averaged selectivities are used: $\langle e \rangle = 0.001, 0.005, 0.01, 0.02, 0.05, 0.08, 0.1, 0.12$. When the asymmetry parameter is smaller than unity a strong universality can be seen. The plots (a)–(d) show the situation for different block length ratios: $p_A = 0.5, 0.6, 0.8, 1.0$. For larger block asymmetries both "wings" of the plots become more asymmetric too. But there is a limiting case for $p_A \to 1$ given in (d). The leading Γ scaling can be represented in the function $g^{\pm}(\Gamma, p_A)$ as given in Eq. (33).

The four parts of Fig. 8 demonstrate this in detail for $p_A = 0.5$, 0.6, 0.8, and 1.0, respectively. Note that the limit $p_A \to 1$ has been taken keeping a and b finite. The depth of the free-energy minimum $\Delta F_{min}(\Gamma)$ normalized to the symmetric case $\Delta F_{min}(0)$ is plotted against the asymmetry parameter $\Gamma = \Delta e / \langle e \rangle^2$. Eight different values of $\langle e \rangle$ are chosen for the different curves. Up to an asymmetry parameter value of order unity a universal behavior is obtained. This is predicted by Eq. (33). Note also the strong decay of the minimum depth in

that range. For larger values of Γ the behavior becomes nonuniversal for different $\langle e \rangle$ as expected.

Comparison of the four plots shows the influence of the block length asymmetry controlled by p_A. The decay for positive asymmetry parameters becomes stronger for increasing p_A. This is especially pronounced in the universal region $\Gamma < 1$.

It is worth noting that the limiting case set a finite correction for that deviation. So the behavior for all different p_A values are located in a finite stripe between
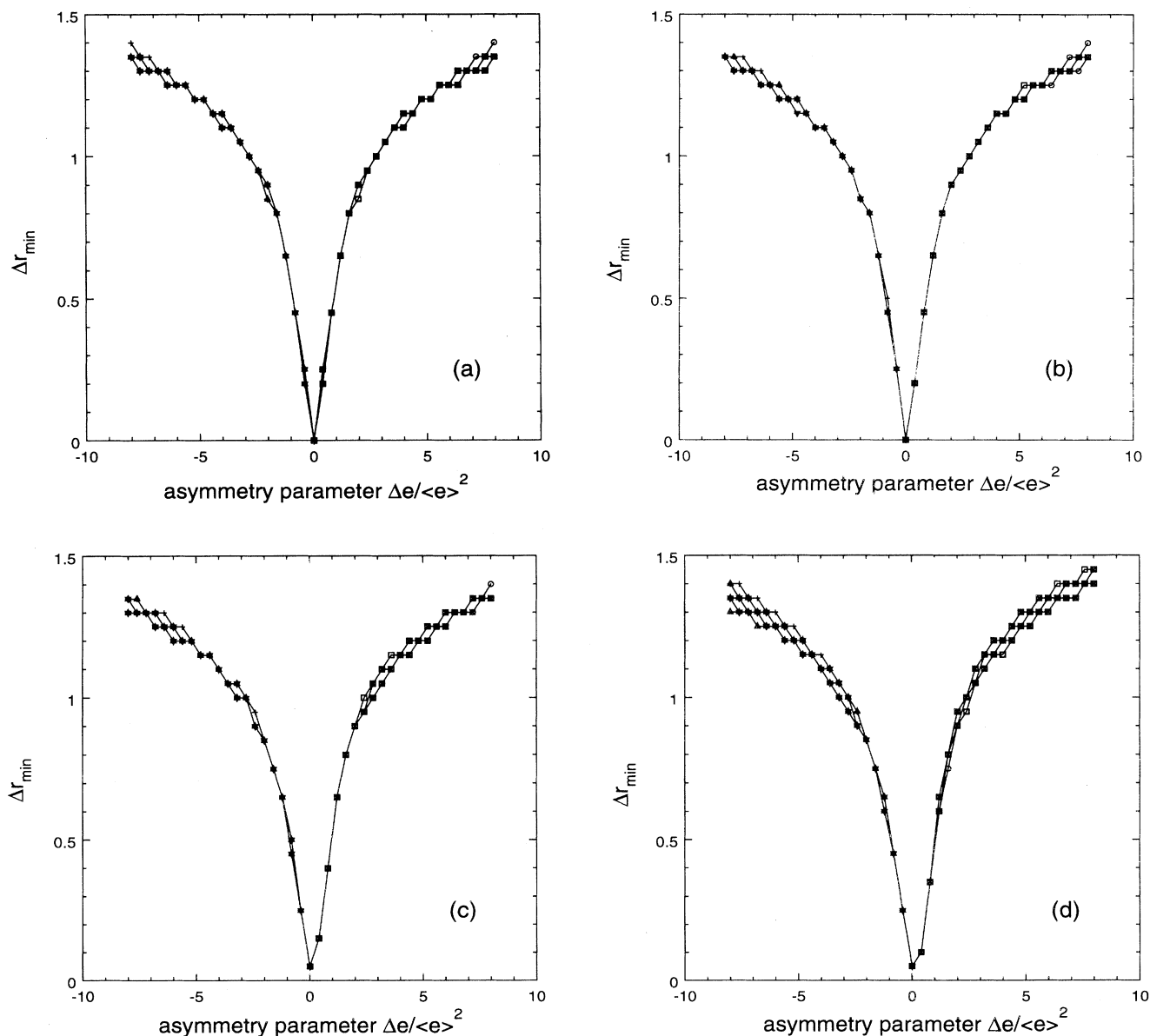

FIG. 9. Same as in Fig. 8 except for the position of the free-energy minimum. Again the leading scaling for the shift of the position minimum is given by a function $h^{\pm}(\Gamma, p_A)$, Eq. (31). For $r_{min}/R > 1$ the curves diverge from each other. The minimal resolution of $\Delta r = 0.05$ of the numerical calculation is visible in that case. If block asymmetry is present, too, the shift is smaller if the shorter block is more repelled by the interface.

$p_A = 0.5$ and $p_A \to 1$ if a and b are fixed. Hence, the quality of the p_A dependence is not the same as for the a-b scaling; see also Fig. 10.

The next set of plots in Fig. 9 shows the shift of the free-energy minimum for the same parameters as in Fig. 8. Since ΔF is calculated on a lattice with spacing 0.05 the minimum calculation cannot be more precise. This is particularly visible for larger asymmetry parameters. Again, in the universal region ($\Gamma < 1$) a pure Γ scaling is predicted; see Eq. (31).

Block asymmetry ($p_A \neq 1/2$) results in two effects. First, even for the case $a = b$ the minimum of ΔF is shifted. This can be seen for $p_A > 0.6$. Second, the minima are less shifted for positive asymmetry than for negative ones. The points for $\Gamma = 0.4$ in Figs. 9(c) and 9(d) clearly show this. Note that for positive asymmetry and $p_A > 1/2$ the *shorter* blocks are repelled more by changing the solvent.

For fixed values of the parameter Γ, the free-energy minimum should scale as $\langle e \rangle^2$; see Eq. (33). This is shown in Fig. 10. Six functions are plotted corresponding to the asymmetry parameter values of 0, 0.4, and 4.4 for the cases $p_A = 0.5$ and $p_A \simeq 1$, respectively. One can see that the block structure changes only very slightly the minimum value of the free energy if the asymmetry

parameter is small. In contrast, if the asymmetry parameter is much larger than unity a remarkable splitting of the graphs can be found. This is shown by the two lower lines in Fig. 10, which both correspond to the asymmetry parameter value of $\Gamma = 4.4$.

C. Adsorption phase diagram

In analogy to Sec. III C we will consider the adsorption crossover of the whole copolymer chain now in the general case. Due to the renormalization procedure described in Sec. II it is mapped into a homopolymer adsorption problem. Each renormalized monomer is a diblock of size R and is subjected to an effective interface potential $\Delta F(r)$.

The difference with Sec. III C consists in the asymmetric potential form of $\Delta F(r)$, see Figs. 5-7. Since we are not interested in details for scales smaller than R we can make use of a simplified model for the function $\Delta F(r)$ as given in the left part of Fig. 11. The two characteristic parameters are the depth of the minimum $\epsilon = \Delta F_{\min}$ and the height of the potential step Δe. It is further possible to establish a continuous model for the renormalized chain. In that case the potential box can be considered as a δ distribution of intensity ϵR. This is sketched in the right-hand side of Fig. 11. It takes the form

$$U_{\text{loc}}(r) = -\epsilon R \delta(r) + \Delta e \Theta(r). \qquad (35)$$

The problem is now the adsorption of a homopolymer chain in a pseudo-potential near a repulsive potential wall. Note that the adsorption problem of polymers near solid surfaces is of the same nature but with an infinitely high potential wall. Note that for the present problem both the adsorption potential *and* the potential
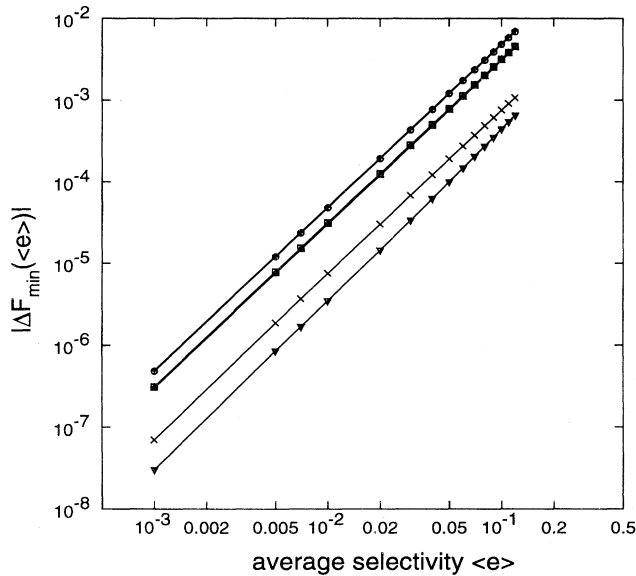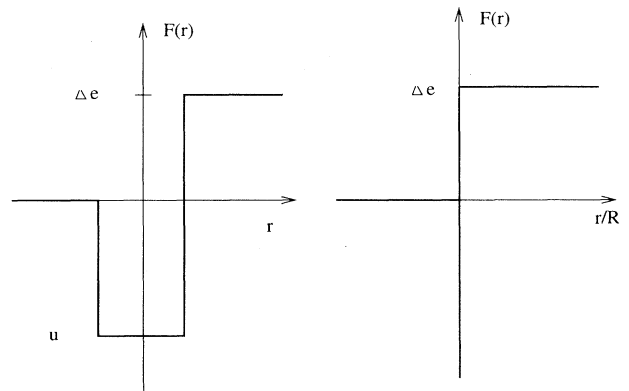

FIG. 10. Depth of the free-energy minimum as a function of the average selectivity strength for different asymmetry parameters and block ratios. The upper two curves, which coincide completely, have zero asymmetry. p_A has the extreme values of $1/2$ and 1, respectively. A slide splitting is visible for the value $\Gamma = 0.4$ of the asymmetry parameter in the middle pair of curves. For an asymmetry parameter of $\Gamma = 4.4$ a difference between $p_A = 1/2$ and $p_A \to 1$ is very clear. The slope of all curves is close to 2. This is an exact result for zero asymmetry.

FIG. 11. Simplified adsorption energy profile. On the left-hand side we show the adsorption profile by averaging over distances of order R. The profile is a combination of a step function of height Δe and a potential box of depth ϵ and width R. The right-hand side shows the profile by going over to a continuous chain. The potential box goes over to a δ profile.

wall have small values.

The adsorption free energy for the chain starting at the interface in the first order of perturbation expansion in respect to $U_{\mathrm{loc}}(r)$ is

$$F_{\mathrm{ad}} \simeq -\epsilon f^{1/2} + \tfrac{1}{2}\Delta e f \quad , \tag{36}$$

where we have suppressed constant factors in the first term. Note that this is the same expression as the corresponding de Gennes approach gives.

As far as the absolute values of both terms in F_{ad} are small the perturbation expansion is good. When the above expression is comparable to the translational free energy of the chain it will adsorb at the interface. At the same time the expansion term cannot be considered as small anymore and the whole series is expected to diverge. The statistics of the adsorbed chain is not only a small perturbation of the statistics of the unperturbed free chain after the adsorption crossover. This argument leads to the usual crossover condition (units of $k_B T$):

$$|F_{\mathrm{ad}}| \simeq 1. \tag{37}$$

However, the difference with the usual adsorption problem is the competition of the the two terms in Eq. (36). Formally F_{ad} is always repulsive for large enough values of f. Figure 12 displays the situation. Generally two cases have to be distinguished depending

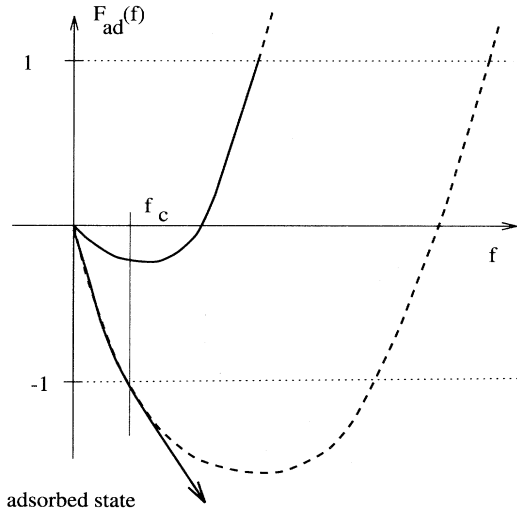on whether the minimum of $F_{\mathrm{ad}}(f)$ is deeper than -1 or not.

If the minimum is shallower than -1 the upturn starts before adsorption can occur. Hence in that case *adsorption is not possible for all chain lengths f*. This is also visible from the general solution of Eqs. (36) and (37) giving the adsorption crossover:

$$f_c^{1/2} = \frac{\epsilon}{\Delta e}\left(1 - \sqrt{1 - \frac{2\Delta e}{\epsilon^2}}\right) \quad . \tag{38}$$

If the expression under the square root is smaller than zero there is no solution of the adsorption equation, the minimum of $F_{\mathrm{ad}}(f)$ is higher than -1; see Fig. 12. Since $\epsilon = \Delta F_{\min}$ scales like the square of the average selectivity [see Eq. (33) and Fig. 10], we get the following *necessary adsorption condition*:

$$\Delta e \ll \langle e \rangle^4 \quad . \tag{39}$$

This means that the asymmetry of the solvent selectivity has to be small for the fourth order to allow for adsorption. This defines the adsorption phase diagram in the $\langle e \rangle$-Δe plane given in Fig. 13. Only the states located in the cone allow for adsorption.

We consider now the situation when the above adsorption condition is fulfilled. The function $F_{\mathrm{ad}}(f)$ in Fig. 12 crosses the line $F_{\mathrm{ad}}(f) = -1$. The corresponding crossover chain length is given by Eq. (38).

For chain lengths larger than f_c the polymer will be adsorbed, i.e., it adopts a flat shape around the interface.

As discussed in Sec. III C the adsorbed chain can be considered as a two-dimensional chain of adsorption blobs of mass g and size W. These adsorption blobs are just "critical," i.e., $g \sim f_c$ and $W \sim f_c^{1/2}$. Since each adsorption blob contributes $k_B T$ (or unity in our convention) to the adsorption free energy one gets for $f > f_c$ simply

$$F_{\mathrm{ad}}(f > f_c) \sim -f/f_c \quad . \tag{40}$$

FIG. 12. The adsorption free energy $F_{\mathrm{ad}}(f)$ as a function of the chain length f according to Eq. (36) for two cases of the parameter $\Delta e/\epsilon^2$. For $\Delta e/\epsilon^2 < 1/2$ adsorption is not possible for any chain length. For large chain length the interface will be repulsive. If $\Delta e/\epsilon^2 > 1/2$ the function crosses the line -1 at the crossover chain length f_c. Due to the adsorption crossover the number of monomers at the interface is proportional to f; see Eq. (41). The adsorption energy decays linearly for $f > f_c$. This is shown by the solid arrow. The rest of the function F_{ad} in Eq. (36) will be no more a proper solution for the adsorbed chain (dashed line).
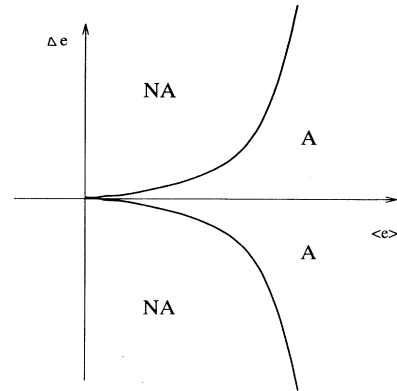
FIG. 13. An adsorption phase diagram. The adsorbable states **A** are inside the cone. Outside the cone adsorption is not possible in the weak selectivity limit **NA**. Both curves are given by Eq. (39).

This implies that the function $F_{ad}(f)$ goes over from Eq. (36) into Eq. (40) when the chain length is crossing the adsorption condition (solid arrow in Fig. 12).

As a consequence the number of chain units directly at the surface f_s increases linearly with f past the adsorption crossover:

$$f_s(f > f_c) = f_c^{1/2} \frac{f}{f_c} = f_c^{-1/2} f \quad . \tag{41}$$

V. DISCUSSION

We have shown that adsorption of multiblock copolymers at interfaces between weakly selective solvents is generally governed by four control parameters, the average selectivity $\langle e \rangle$, the selectivity asymmetry parameter $\Gamma = \Delta e / \langle e \rangle^2$, the block length ratio p_A, and finally the number of diblocks f. The first three parameters determine a unique free-energy profile for a single diblock near the interface.

We found in Sec. IV C that adsorption at weakly selective interfaces is very sensitive to the asymmetry of the copolymer-solvent system. Only very close to the symmetry condition $\chi_A n_A = \chi_B n_B$ is adsorption possible; see also Fig. 13. In that case the effective interface attraction ϵ of an individual diblock scales as $\langle e \rangle^2$.

The crossover chain length in units of diblocks is given by Eq. (38) in the general case. For small ratios $\Delta e / \epsilon^2$ the results of Table I are reproduced.

Equation (38) predicts a largest adsorption blob size f_c^{max}. If the square root is zero f_c remains finite for $\Delta e > 0$:

$$(f_c^{max})^{1/2} = \frac{\epsilon}{\Delta e} = \frac{1}{\Gamma} \quad . \tag{42}$$

Larger blobs would be unstable because of the repulsion due to the potential step.

Note that this behavior is quite different from the case of adsorption onto solid surfaces. A solid surface would correspond to an infinite potential step in Eq. (35). This cannot be treated by a naive perturbation expansion as the corresponding critical adsorption energy ϵ_c is not small compared to $k_B T$. For an ideal chain it takes a value of $\ln(2)$. The chain configuration is completely different from the one considered in our case. There can be no monomers in the other half space hence also the blobs are half-space blobs. If ϵ is larger than ϵ_c the adsorption blobs can be arbitrarily large [8].

The crossover between both cases by increasing the potential step and the attraction energy to larger values is an interesting problem but goes beyond the scope of the present work.

The main conclusions of this work can be summarized as follows.

(i) Multiblock copolymer chains can be adsorbed at weakly selective interfaces due to a polarization effect of the individual diblocks. This results in the usual ho-mopolymer adsorption at a *penetrable interface.*

(ii) If the selectivity of both solvents is asymmetric with respect to both monomer sequences adsorption is only possible if the asymmetry is very small compared to the average attraction ϵ of the solvent-solvent interface. This defines a *critical value* ϵ_c *for a given asymmetry* Δe.

(iii) When asymmetry is present and $\epsilon > \epsilon_c$ the *largest adsorption blob is finite.* This is a qualitatively new effect of the weakly selective solvent-solvent interface compared to other polymer adsorption problems.

(iv) Due to the very *sensitive dependence on asymmetry,* the solvent selectivity of such interfaces can be used to select narrow distributions of multiblock chain architectures.

APPENDIX A: DERIVATION OF THE EFFECTIVE POTENTIAL

The starting point here is the equation for the ideal propagator G of the copolymer chain with the potential given in (2):

$$\dot{G} = D\Delta G - U(\mathbf{R})b(t)G \quad , \tag{A1}$$

where D is given by $D = l^2/6$.

First, an ansatz is produced by solving the above equation without the "connectivity" term $D\Delta G$.

The truncated equation takes the form

$$\dot{G}_t(\mathbf{R}, \mathbf{R}'; t) = U(\mathbf{R})b(t)G_t(\mathbf{R}, \mathbf{R}'; t) \quad , \tag{A2}$$

where the index t in G_t denotes that this is only a partial solution for G. The solution is given by

$$G_t(\mathbf{R}, \mathbf{R}'; t) = g \exp\left(-\int_0^t b(t')dt' U(\mathbf{R})\right) \quad , \tag{A3}$$

where g is a constant for the reduced equation. Note that this partial solution makes sense only if $b(t)$ is a periodic function with equal weight for both signs. Otherwise, the integral appearing in Eq. (A3) diverges for large t and hence, G_t has no finite value. On the other hand, if $b(t)$ is periodic with a finite integral G_t is also periodic and fluctuates as fast as the potential. The idea is that for large t values there exist also a slowly varying function, which we call $g(\mathbf{R}, \mathbf{R}'; t)$. This function is distorted by G_t only on small t scales. Note that the solution of (A3) oscillates around unity for the given restrictions. Thus we make an ansatz in the following form:

$$G(\mathbf{R}, \mathbf{R}'; t) = g(\mathbf{R}, \mathbf{R}'; t)G_t(\mathbf{R}, \mathbf{R}'; t). \tag{A4}$$

Substituting this in Eq. (5) we obtain

$$\dot{g} = D\Delta g + DF^2(t)(\nabla U)^2 g + DH'g, \tag{A5}$$

with

$$H' = -F(t)\left(\Delta U - 2\nabla U \nabla\right) \quad . \tag{A6}$$

Here the symbol $F(t) = \int_0^t b(t')dt'$ has been introduced. The above equation is in principle more complicated as the original one [Eq. (A2)] but contains also the proper solution. However, only the second term in Eq. (A5) provides a square in the periodic function $F(t)$. By preaveraging over the periodic fluctuation $F(t)$ this is the only term that survives. Since this result is already nontrivial we can try it as a first approach. However, one needs to check the "stability" of this preaveraging procedure by calculating perturbatively the contributions arising from the remaining terms [4,5]. Using the chemical block structure function $b(t)$ of the copolymer given by Eq. (3) the effective equation for the slow part takes the final form:

$$\dot{g} = D\Delta g + \frac{1}{48}Dn^2\left(\nabla U\right)^2 g \quad . \tag{A7}$$

This defines an effective t-independent potential. By using this approach one has to realize the restriction to $2T\max[|U(x)|] < 1$. Otherwise the function G_t given by Eq. (A3) takes very large and very small values and the picture of the slightly disturbed function g is wrong, hence the approximation presented here.

On the other hand, for sharp potentials when the width becomes comparable to the wavelength of the fluctuation this approach breaks down. This has already been discussed in the original papers [4,5]. In this case the contributions due to H' become important.

APPENDIX B: INDUCED DIPOLE APPROACH

For the full symmetric case we have treated the weak selectivity problem for an ideal chain rigorously (within the scale R). The main physical results concern the scaling of $\langle F\rangle$ with u, n, and w. Additionally we gave an interpolation formula and an alternative approach for the smooth potential. We will now present an alternative way to understand the above results using an *ad hoc* dipole model for a single diblock [11]. This will provide the same scaling results in a much easier way and is useful for the understanding of the physics behind the above results.

Let us consider a single diblock copolymer as a pair of two monomer clouds interpenetrating each other. Without a selective potential the average distance vector between the centers of mass of the two blocks in the di-

rection perpendicular to the interface is zero. However, when we place it in a selective potential the two clouds will be separated. This yields a nonvanishing average of the separation vector perpendicular to the selective interface. We will denote this displacement by Δx. This separation involves an elastic free energy F_{el} of the stretched diblock. It has the usual form, $F_{\text{el}} = 1/2(\Delta x)^2/R^2$. Due to the stretching the diblock gains a certain selectivity energy E. The latter may be written as the product of the excess of the number monomers in their preferred solvent Δn due to the stretching and the average amount of energy per monomer $\langle U\rangle$. Hence $E = \Delta n\langle U\rangle$. The free energy of the diblock is given by

$$F = F_{\text{el}} + E \quad . \tag{B1}$$

The amount of "satisfied" monomers due to the stretching will be proportional to the gained area ΔA. Since we consider only a weak deformed ellipsoid we have $\Delta A = \Delta x R$. So we get $\Delta n = (\Delta A/A)n = n\Delta x/R$. The above equation takes the form

$$F = \frac{1}{2}\frac{(\Delta x)^2}{R^2} + \frac{\Delta x}{R}n\langle U\rangle \quad . \tag{B2}$$

Minimization of the free energy yields the average of F gained by the selective potential:

$$\langle F\rangle \sim -n^2\langle U\rangle^2 \quad . \tag{B3}$$

For the case of sharp selectivity $\langle U\rangle$ is simply equal to u and we get (up to constants) the same result as in Eq. (15).

If the interface potential has the general structure of Eq. (4) we get

$$\langle U\rangle = -2\frac{1}{R}\int_0^R \chi \tanh(x/w)dx$$
$$= -2\chi\frac{w}{R}\ln\cosh(R/w) \simeq -2\chi\frac{R}{R+w}. \tag{B4}$$

Hence we get for the general case,

$$\langle F\rangle \simeq -4n^2\chi^2\left(\frac{R}{R+w}\right)^2 \quad . \tag{B5}$$

APPENDIX C: SECOND-ORDER CONTRIBUTION IN THE ASYMMETRIC CASE

We have to evaluate Eq. (10) for the potential given in Eq. (1). First, it is useful to split the arclength integration into three parts in the following way:

$$\int_0^n dt\int_0^t ds = \left(\int_0^{n_A}dt + \int_{n_A}^n dt\right)\int_0^t ds = \int_0^{n_A}dt\int_0^t ds + \int_{n_A}^n dt\int_0^{n_A}ds + \int_{n_A}^n dt\int_{n_A}^t ds \quad . \tag{C1}$$

Now in all three terms the potentials $V_{A,B}$ belong to a definite species and we can use Eq. (1). It is further useful to reduce all arclength and spatial scales by n and $\sqrt{n}$, respectively. Especially we recall the previous definition of $p_{A,B} = n_{A,B}/n\ (p_A + p_B = 1)$.

Hence, the expression for $\langle V^2\rangle_0$ has three contributions of the form

$$\langle V^2 \rangle_0 = 4a^2 \frac{1}{p_A^2} I_1(p_A, r) + 4b^2 \frac{1}{(1 - p_A)^2} I_2(p_A, r) + 4ab \frac{1}{p_A(1 - p_A)} I_3(p_A, r). \tag{C2}$$

The three integrals take the form

$$I_1(p_A, r) = \int_0^{p_A} dt \int_0^t ds \int_0^{-\infty} dz \, \mathrm{erf}\left(\frac{z}{\sqrt{2s}}\right) G(2z - 2r, 1 - s), \tag{C3}$$

$$I_2(p_A, r) = \int_0^{p_B} dt \int_0^t ds \int_0^{\infty} dz \, \mathrm{erf}\left(\frac{z}{\sqrt{2s}}\right) G(2z - 2r, 1 - s), \tag{C4}$$

$$I_3(p_A, r) = \int_{p_A}^1 dt \int_0^{p_A} ds \int_0^{-\infty} d\Delta x \, G(\Delta x, t - s) S_{\mathrm{ef}}[\Delta x, r, 1 - (t - s)]. \tag{C5}$$

The function $S_{\mathrm{ef}}(x, y, s)$ is introduced as follows:

$$S_{\mathrm{ef}}(x, r, s) = \frac{1}{2}\left\{ \mathrm{erf}\left(\sqrt{\frac{2}{s}}(x + r)\right) + \mathrm{erf}\left(\sqrt{\frac{2}{s}}(x - r)\right) \right\}. \tag{C6}$$

Let us consider the limiting case of very small ratios of the block length, i.e., $p_A \simeq 0$ or $p_A \simeq 1$, respectively, but finite values of a and b. Both cases are equivalent by switching the sign of r. We take $p_A \to 1$. We start with the first integral given by Eq. (C3). The limits p_A can be set to unity. The second integral, see Eq. (C4), contains a double arclength integration with very small limits. Hence, the result of the z integration can be considered as constant at the point $s = 0$. Note that the result of the double arclength integration is given by $p_B^2/2$. The square of p_B cancels just the corresponding prefactor. The whole integral can be treated exactly. In the third integral [Eq. (C5)] the t integration can be treated also in this way and the s integration extends to unity. All together we obtain for $p_A \to 1$:

$$\frac{1}{p_A^2} I_1(p_A, r)^{p_A \to 1} = \int_0^1 dt \int_0^t ds \int_0^{-\infty} dz \, \mathrm{erf}\left(\frac{z}{\sqrt{2s}}\right) G(2z - 2r, 1 - s), \tag{C7}$$

$$\frac{1}{p_B^2} I_2(p_A, r)^{p_A \to 1} = \frac{1}{2}\int_0^{\infty} dz G(2z - 2r, 1) = \frac{1}{8}[1 + \mathrm{erf}(\sqrt{2}r)], \tag{C8}$$

$$\frac{1}{p_A p_B} I_3(p_A, r)^{p_A \to 1} = \int_0^1 ds \int_0^{-\infty} d\Delta x \, G(\Delta x, 1 - s) S_{\mathrm{ef}}[(\Delta x, r, s)]. \tag{C9}$$

Note that the limiting process, of cause, eliminates the explicit appearance of p_A (p_B).

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[1] Copolymers consisting of hydrophylic and hydrophobic monomers dissolved in an oil-water emulsion are a common known example.

[2] The above approach produces generally a potential dependent R value: $R' = R + \Delta R(r)$ and also a coupling of the directions of two successive monomers: $a(r)(t_i t_i + 1)$ with $t_i = r_{i+1} - r_i$. In the present case of weak selectivity we neglect both of them.

[3] Actually the individual block may be stretched in the saturated surface regime. That means the layer width W scales as n instead of $W \sim n^{1/2}$ for an unconstrained chain. However, we do not go into the details of this regime. See E. Leclerc, M. Daoud, and R. Douillard, Nuovo Cimento **15**, 641 (1994).

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[6] Note that the de Gennes approach [7] is the same as the perturbation expansion with respect to the effective adsorption potential per monomer. The reason is that the adsorption potential is considered as a weak effect that does not really deform the chain configuration. The crossover is then simply given by the condition where this approach breaks down.

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[10] This is especially interesting in the case of real chains. Here the cross-over exponent ϕ is expected to be different for the case of penetrable and nonpenetrable interfaces, respectively.

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