

## Adsorption and desorption of reversible supramolecular polymers

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We report numerical mean-field results on the quasichemical level of approximation that describe adsorption of reversible supramolecular polymers at a flat interface. Emphasis is laid on the regime of strong adsorption from a dilute solution. There are two differences with respect to macromolecular polymer adsorption: (i) adsorption sets in at relatively high monomer concentrations of the surrounding solution, and (ii) the surface is filled within a much narrower concentration range. Contrary to macromolecular polymers, supramolecular polymers can therefore be desorbed by dilution of the equilibrium solution by solvent within an experimentally accessible concentration window. Based on simple thermodynamic arguments, we provide a quantitative explanation why supramolecular polymers adsorb at relatively high concentrations. Moreover, we discuss the (by comparison) narrow concentration window wherein filling of the surface occurs. This is attributed to the cooperative nature of supramolecular polymer adsorption. The degree of cooperativity is quantified by means of the Hill parameter  $n$ .

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### I. INTRODUCTION

Polymers play a central role in molecular biology and are essential in many industrial processes as well. This has contributed to the emergence of various scientific activities to unravel the properties of polymeric compounds since the 1920s. The study of *reversible supramolecular polymers* (also known as *living polymers*) is a relatively recent branch of this diverse field of research. Supramolecular polymers are reversible aggregates consisting of monomers that form linear and/or ring-shaped structures. Solutions of supramolecular polymers usually contain a broad chain length distribution. However, it is not the polydisperse nature as such that sets them apart from regular polymers. Rather, it is their ability to adjust the chain lengths as a response to externally imposed stresses.

Numerous compounds can be classified as “supramolecular polymers.” The best studied system is probably cetylammmonium bromide, a surfactant that forms semiflexible cylindrical micelles in the presence of sodium or potassium ions [1,2]. Other examples of compounds that exhibit supramolecular polymer behavior are liquid sulphur [3], selenium [4], actin filaments [5], and specially designed synthetic monomers [6]. The latter group is usually categorized according to the nature of the reversible bond between the monomers [6]: hydrogen-bonded [7], discotic [8], and coordination [9] supramolecular polymers. The effort made to produce synthetic supramolecular polymers in recent years has paved the way for validation of many existing theories.

Supramolecular polymers have already surpassed the stage of a mere scientific curiosity or a theorists’ toy. They are regarded as highly promising for technological and industrial applications [6,10]. The possibility to reversibly alter the mean chain length *in situ* (e.g., by applying shear or changing the temperature) makes supramolecular polymers a

very promising candidate for numerous applications (e.g., nanotechnology [10]) since the rheological properties of the system can be tuned.

Moreover, polymers in general are very important in inhomogeneous systems, where they are used to control the stabilization of colloidal suspensions [11], prevent biofouling [12], etc. By using supramolecular polymers, it is to be expected that the properties of these systems can be adjusted in a more refined way compared to ordinary polymers. It is therefore of interest to predict to what extent supramolecular polymers adsorb to a surface and how they alter the properties of such a surface.

Several studies of supramolecular polymers near nonadsorbing [13–20] and adsorbing [19–21] interfaces were reported in recent years. It was predicted that supramolecular polymers behave more or less similarly to ordinary polymers near interfaces. They are depleted from the interface region for entropic reasons if no favorable energetic interaction occurs for a contact between the polymer and surface. Furthermore, long chains exhibit thicker depletion layers than short chains, which was also predicted for bidisperse classical polymers [22,23]. Adsorption takes place only when favorable energetic interactions compensate the entropy loss.

All these phenomena are also found in systems that contain ordinary polymers. However, in a recent paper we presented adsorption isotherms from which it can be inferred that for a realistic set of parameters supramolecular polymers may not adsorb unless the volume fraction of monomers in solution is higher than about  $10^{-6}$  [24]. Put in a different way, supramolecular polymers may be desorbed from a surface in that case if the concentration of the surrounding solution is decreased below  $10^{-6}$ , which is well within the experimental range [25]. This behavior is virtually never found for macromolecular polymers, which can normally not be desorbed to a significant extent by just diluting the surrounding solution [25].

It is to be expected that this profound difference will have important implications in the applicability of supramolecular polymers as surface-modifying agents, because the adsorbed layer can be easily removed by diluting the solution. Since

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one of the proposed applications of supramolecular polymers is surface modification, it is of interest to study this effect in more detail.

Here we present a systematic study that assesses the effects of varying the model parameters on the adsorption behavior of supramolecular polymers. Previous studies in this field have focused on relatively high concentrations [21] or employed theory that is not particularly well suited to study supramolecular polymers at low concentrations (and hence low aggregation numbers) [19,20]. We will focus on the regime of low monomer concentrations, since this is the relevant regime to study desorption.

Many of the quantitative results presented in this paper are applicable to the situation where the adsorbed molecules are confined to a thin layer adjacent the surface. This is known as the “train” regime because the adsorbed material resides in trains [24]. This is a relevant regime for desorption, since any layer of adsorbed polymers is flat, provided that the concentration of molecules in the surrounding solution is sufficiently low and adsorption is strong enough. The train regime is especially important when the adsorption contribution per segment is strong. As in our previous paper [24], we will therefore focus on the strong-adsorbing case.

This paper is organized as follows. First, the model is described that was used to study the adsorption of supramolecular polymers. Then, in Sec. III, we compare the adsorption isotherms of supramolecular and macromolecular polymers in general terms. Sections IV and V each address a profound difference in adsorption behavior between the two types of polymer. The paper is concluded by summarizing the results and providing recommendations for experimental systems (Sec. VI).

## II. DESCRIPTION OF THE MODEL

We use a cubic lattice model to study the properties of the adsorbed layers of supramolecular polymers in more detail. There are several reasons to choose a discretized model. In comparison with continuum models, lattice models (i) tend to be computationally less demanding, (ii) are easily analyzed, and (iii) allow a very simple and straightforward definition of supramolecular polymers (Fig. 1). The main disadvantage of using a lattice model in this case is probably that nematic ordering is not well captured by a discretized approach [26]. However, the focus of this paper is on flexible chains. It is therefore unlikely that a continuum model would lead to qualitatively different conclusions from those presented in this paper.

The same model and notation are used in this paper as in our previous paper [24]. The model is depicted in Fig. 1. Molecules are modeled as cubic particles with different faces. Only nearest-neighbor interactions are taken into account. A contact energy is assigned to each pair of faces on adjacent molecules that point toward each other. All energies are given in units of  $kT$  for simplicity.

At least two types of interaction energies are present in any system containing adsorbed supramolecular polymers: adsorption energy and linking energy. With adsorption energy we hereby loosely mean the energy difference that a

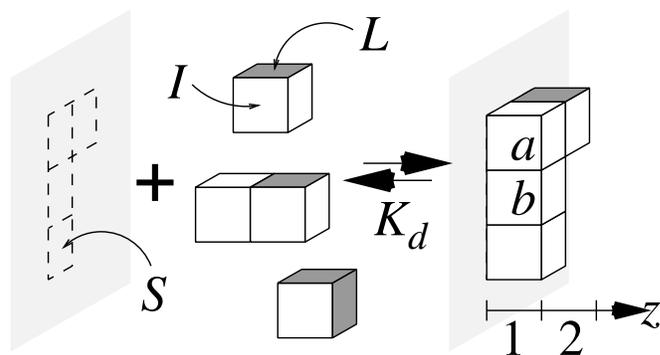


FIG. 1. Schematic representation of the current model. The supramolecular polymers are modeled as strings of monomers, which are connected by faces of type  $L$  (linking faces). Each monomer has exactly two of those faces. The other four faces are of type  $I$  (indifferent faces), and we refer to the faces at the surface as  $S$  (surface faces). The monomers  $a$  and  $b$  belong to two different configurations of the monomer because the linking faces are pointing in different directions. The linking faces are perpendicular in molecule  $a$ . Hence at  $a$  the chain is bent and  $a$  is referred to as a “bent” monomer. The linking faces are parallel in molecule  $b$ , this is therefore a “linear” monomer. The adsorption of supramolecular polymers is viewed as an equilibrium reaction between the surface and the chains in the bulk. The equilibrium constant of the dissociation reaction is  $K_d$ . Solvent molecules (not depicted) are modeled as monomeric, isotropic species without net energetic interaction with monomers or the wall. The spatial coordinate  $z$  measures the distance perpendicular to the surface:  $z=1$  next to the surface and  $z$  is normalized so that the lattice spacing is equal to unity. The assembly of lattice sites at a certain integer value of  $z$  forms a *lattice layer*.

monomer experiences as it is transferred from the bulk to the surface. The adsorption is governed by the parameter  $u_{IS}$ , which is the energy that is assigned to each contact between an indifferent face  $I$  and the surface  $S$  (see Fig. 1). In the present study, this energy difference is sufficiently negative; otherwise, the polymers are depleted from the surface.

Moreover, a linking energy  $u_{LL}$  is assigned to every contact between two linking faces  $L$  (see Fig. 1). A reversible bond between two monomers is formed when two linking faces on each monomer are in contact. Therefore  $u_{LL}$  may also be seen as the bond energy. The bond energy has to be sufficiently negative for achieving appreciable chain formation. In literature, often the scission energy is used as the parameter that controls chain formation [1]. The scission energy is directly related to  $u_{LL}$ :  $E_{scission} = -u_{LL}$ . Apart from  $u_{IS}$  and  $u_{LL}$ , all contact energies are set to zero.

We can assign a *bending penalty*  $u_{bent}$  to states of monomers where the linking faces are perpendicular with respect to each other. By changing  $u_{bent}$ , we can change the flexibility of the polymer chain. It is straightforward to show that the persistence length  $\ell_p$  in a cubic lattice is equal to  $\ell_p = 1 + \frac{1}{4} \exp(u_{bent})$  [27,28]. In this paper,  $u_{bent}$  was set to zero (flexible chains) unless stated otherwise.

The internal energy of a system is therefore determined by the occupation of molecules, the orientation of the faces, and the set of energy parameters  $u_{IS}$ ,  $u_{LL}$ , and  $u_{bent}$ . These param-

eters are referred to as a set  $\{u\}$ . Given  $\{u\}$  and the overall monomer concentration  $\phi$ , we must find the distribution of monomers over the system. Grand canonical Monte Carlo simulations could in principle be used to find the occupation of the lattice sites. These calculations yield “exact” results when applied properly. However, it turns out that Monte Carlo methods are unsuitable if realistic bond energies are applied. Realistic bond energies of triple- or quadruple-hydrogen-bonded monomers are in the order of  $-10$  to  $-20$  [6]. Such strong interactions lead to excessive equilibration times in Monte Carlo calculations. As in our previous paper, we will therefore use a numerical technique that is virtually unrestricted in parameter choice. By means of this technique, the average occupation of the lattice sites is calculated on the level of the quasichemical approximation [29]. Some 20 years ago, it was shown that computations at this level yield far better results in describing the equation of state of chain molecules than random-mixing theories [30]. Yet it can handle very low concentrations and strong interactions while the computational demands remain modest. Since the partition functions and minimization scheme are readily available in literature [16,29], they are not repeated here.

It is instructive to compare the properties of reversible supramolecular polymers with irreversibly linked macromolecular polymers. We will use the model proposed by Scheutjens and Fler to describe adsorbed layers of macromolecular polymers on a mean-field level [31,32]. We follow the usual notation for macromolecular polymer adsorption in this paper. The parameter  $\chi$  is the Flory-Huggins polymer-solvent interaction parameter. The adsorption energy per segment is indicated by  $\chi_s$ , which is equal to  $-u_{IS}$ .

### III. GENERAL ASPECTS OF ADSORPTION ISOTHERMS

In the present quasichemical calculation, the surface is infinitely large and completely flat. A chain is adsorbed if at least one monomer of the chain is adjacent the surface. Since a lattice layer represents a certain volume, we can express amounts in terms of equivalent lattice layers. It is convenient to express the adsorbed amounts of monomers in terms of the number of equivalent lattice layers that the monomers of adsorbed chains occupy. Adsorbed amounts are indicated by  $\Gamma$  and can be subdivided in contributions from trains, loops, and tails [24], denoted as  $\Gamma_{tr}$ ,  $\Gamma_{lp}$ , and  $\Gamma_{tl}$ , respectively. The adsorbed amounts plotted against the volume fraction  $\phi$  for a certain choice of parameters  $\{u\}$  are shown in Fig. 2. The isotherms shown in this figure more or less reflect the experimental window. The experimentally accessible region of volume fractions has a lower bound at approximately  $10^{-8}$  [25].

Figure 2 compares the adsorption of supramolecular polymers with macromolecular polymers. The adsorption energy per segment is the same in both isotherms. The number of segments of the macromolecular polymer was arbitrarily chosen to match the length of supramolecular polymers in the melt. It was shown previously [16] that the average chain length  $\langle N \rangle$  of supramolecular polymers in an isotropic, homogeneous environment is given by

$$\langle N \rangle = 1 + \sqrt{\frac{\phi}{q/2 - \phi}} \exp\left(-\frac{u_{LL}}{2}\right), \quad (1)$$

where  $q$  is the coordination number of the lattice ( $q=6$  for a cubic lattice). Equation (1) is exact within the quasichemical

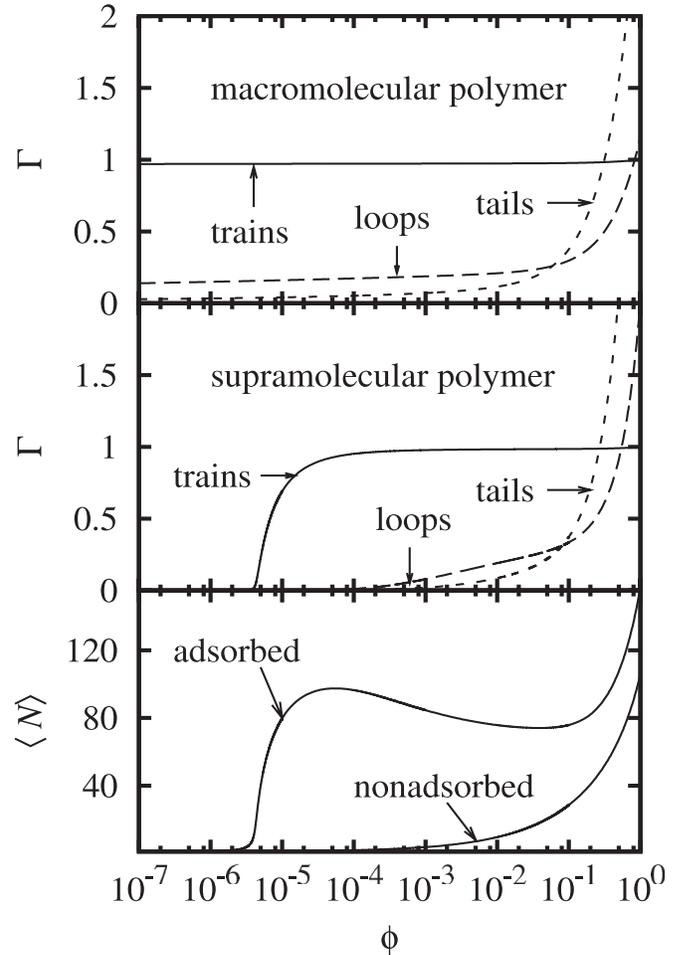


FIG. 2. The top and the middle plot make a comparison between macromolecular and supramolecular polymers. The adsorbed amounts  $\Gamma$  (expressed in equivalent lattice layers) for trains, loops, and tails are plotted against the volume fraction of monomers in the bulk. The trains are confined to the layer adjacent the interface, so  $\Gamma_{tr} \leq 1$ . Bottom plot: mean chain length of adsorbed and nonadsorbed supramolecular polymers. The sudden increase in  $\Gamma_{tr}$  coincides with the sudden increase in the mean chain length of adsorbed supramolecular polymers, which indicates cooperativity of the adsorption process. Parameters:  $N=100$ ,  $\chi=0$ ,  $\chi_s=4$ ,  $u_{IS}=-4$ ,  $u_{LL}=-10$ , and  $u_{bent}=0$ .

approximation. In a polymer melt,  $\phi \approx 1$ ; hence,  $\langle N \rangle$  is then about 100 for the supramolecular polymers shown in Fig. 2. Therefore the isotherm was compared with macromolecular polymers of length 100.

Supramolecular polymers display adsorption behavior which in a number of respects is similar to macromolecular polymers. Trains dominate at low  $\phi$ , and at increasing  $\phi$  first loops are formed, but eventually, at very high concentrations, most of the adsorbed material resides in tails.

However, there are two notable differences between the two isotherms shown in Fig. 2. First, at low  $\phi$  loops are far more prominent for macromolecular polymers than for supramolecular polymers. This is due to the decrease in chain length of supramolecular polymers upon decreasing  $\phi$ : Equation (1) shows that the chain length decreases with decreasing concentration. When stronger bonds are formed ( $u_{LL}$

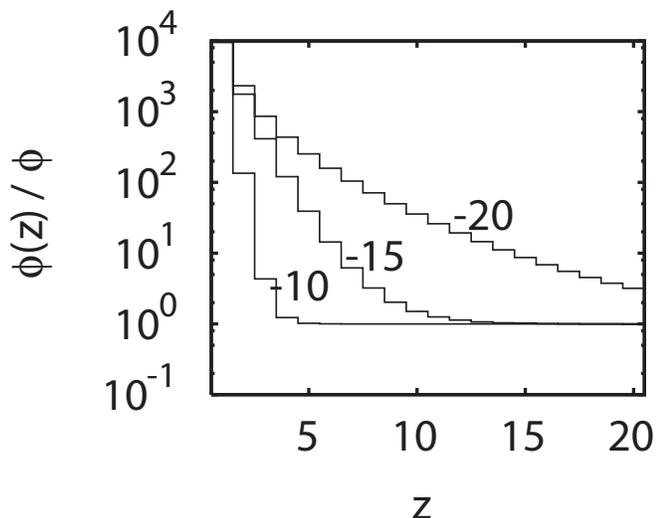


FIG. 3. Concentration profiles of adsorbed supramolecular polymers for different values of  $u_{LL}$ . The ranking number of a layer is indicated by  $z$ , where the surface is on the left. The volume fraction of monomers in layer  $z$  is denoted  $\phi(z)$ . Parameters:  $\phi=10^{-4}$  and  $u_{IS}=-4$ .

more negative), then more extended layers are formed, as is demonstrated in Fig. 3.

The second difference between the isotherms in Fig. 2 is that macromolecular polymers fill almost the entire surface in the entire shown concentration range whereas supramolecular polymers show a buildup of the train fraction only above  $\phi=10^{-5}$  (for this set of model parameters). These results indicate that supramolecular polymers can be desorbed by diluting the solution which is in contact with the surface. To remove macromolecular polymers in this way is very difficult, as was already pointed out by Scheutjens and Fleer in the 1980s [33].

Let us determine how difficult it actually is to desorb macromolecular polymers. For sufficiently low concentrations, adsorbed polymers always consist completely of trains. When one is interested in removing the adsorbed amount entirely, it is imperative to study the train regime. Hence it is sufficient to characterize adsorption by simply the *surface coverage*  $\theta \equiv \Gamma_{tr}$ . The parameter  $\theta$  is equal to the volume fraction of monomers at  $z=1$ . Throughout the rest of this paper, we will refer to plots of  $\theta$  versus  $\phi$  as “adsorption isotherms.”

Adsorption isotherms of macromolecular polymers for several values of  $\chi_s$  are shown in Fig. 4. This plot illustrates that macromolecular polymers desorb only at excessively low concentrations.

The part of the isotherm that is of most interest is the region where the surface sites become occupied to an appreciable extent. We loosely denote this process as “filling of the surface.” Filling of the surface to a appreciable extent requires a change of monomer concentration of many decades in the case of macromolecular polymers, but less than one decade for adsorbing supramolecular polymers.

A physical explanation for this phenomenon is cooperativity: adsorbing supramolecular chains do not only profit

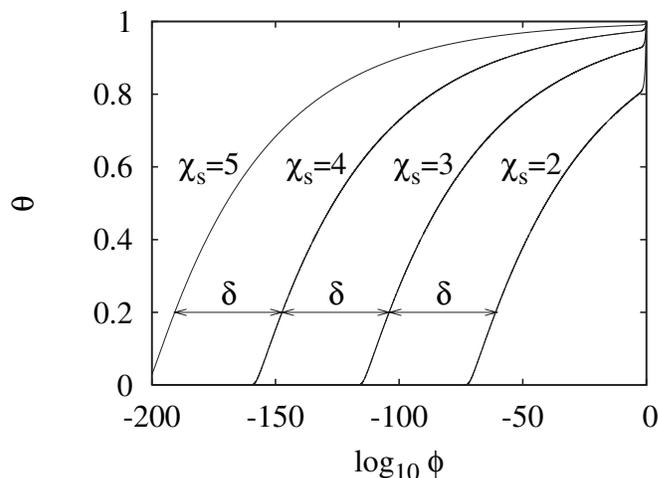


FIG. 4. Adsorption isotherms of macromolecular polymers at different adsorption energies  $\chi_s$ . Parameters: chain length  $N=100$ ,  $\chi=0$ , cubic lattice. A different value of  $\chi_s$  leads to a shift of the isotherm of magnitude  $\delta=\Delta \log_{10}\phi$ . The shift was calculated according to  $\delta=N\Delta\chi_s/\ln 10$ , which assumes strong adsorption.

from *IS* interactions, but also from forming bonds with chains that are already present at the surface. Therefore the increase in  $\Gamma_{tr}$  in Fig. 2 coincides with a large increase in the mean chain length of adsorbed supramolecular polymers. This effect was already observed previously for supramolecular polymers studied by means of an analytical [20] and numerical [24] self-consistent field theory. As a result, adsorption of supramolecular polymers is *enhanced* by the presence of already adsorbed molecules, whereas the adsorption of macromolecular polymers is *hindered* by adsorbed polymers.

Summarizing this section, we state that in comparison with macromolecular polymers, the adsorption isotherms of supramolecular polymers (i) are shifted due to a change in adsorption energy per segment much less along the concentration axis and (ii) exhibit a much steeper increase in  $\theta$  due to the cooperative nature of adsorption. These effects will be discussed separately in the following sections.

#### IV. ISOTHERM SHIFT ALONG THE CONCENTRATION AXIS

The purpose of this section is to give an explanation why supramolecular polymers can be desorbed within experimentally accessible concentrations, whereas this is almost impossible for macromolecular polymers. Adsorption isotherms  $\theta(\phi)$  of macromolecular polymers for different adsorption energies are shown in Fig. 4. A few adsorption isotherms of supramolecular polymers are shown in Fig. 5. Varying  $\chi_s$  or  $\{u\}$  does not change the shape of the adsorption isotherm, but leads to a *shift* of the isotherm along the  $\log_{10}\phi$  axis.

The magnitude of this shift  $\delta=\Delta \log_{10}\phi$  can be found by the consideration that the populations of molecules at the surface and in solution are distributed according to a Boltzmann equilibrium:

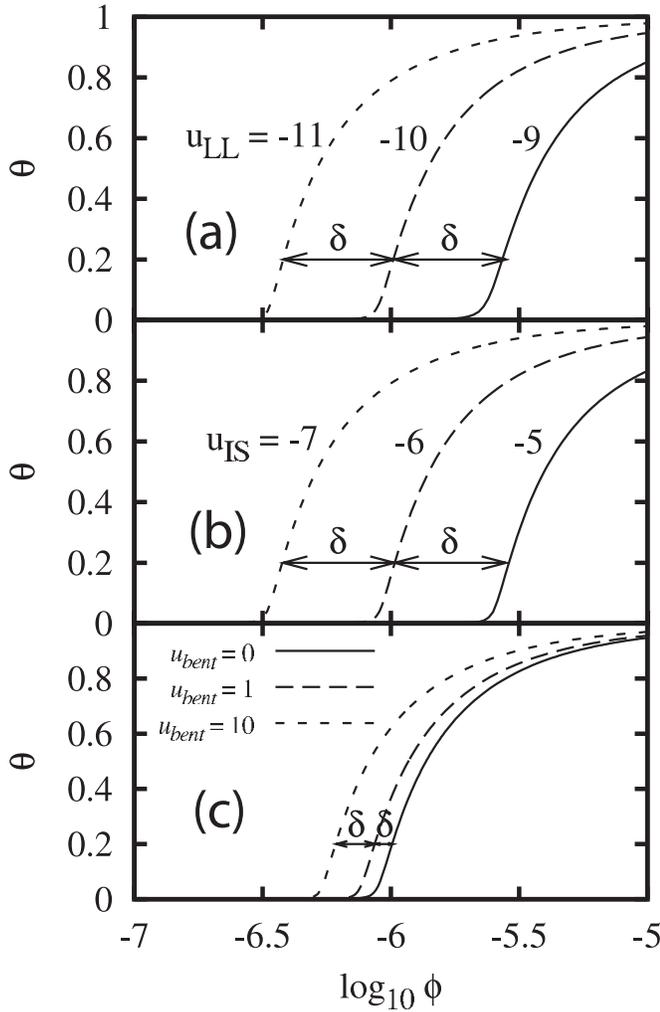


FIG. 5. Adsorption isotherms of supramolecular polymer solutions: plot of surface coverage  $\theta$  versus monomer concentration in the bulk solution  $\phi$ . Plot (a): effect of bond energy. Parameters:  $u_{IS} = -6$ ,  $u_{bent} = 0$ ;  $u_{LL}$  is varied. Plot (b): effect of adsorption energy. Parameters:  $u_{LL} = -10$ ,  $u_{bent} = 0$ ;  $u_{IS}$  is varied. Plot (c): effect of flexibility of the chain. Parameters:  $u_{IS} = -6$ ,  $u_{LL} = -10$ ;  $u_{bent}$  is varied. The shifts of the adsorption isotherms, indicated by  $\delta = \Delta \log_{10} \phi$ , were calculated by means of Eqs. (4) and (7).

$$\frac{\theta}{\phi(\theta)} = e^{-\Delta_{ads}F}, \quad (2)$$

where  $\phi(\theta)$  is the monomer concentration in the bulk solution in equilibrium with a surface with surface coverage  $\theta$ . In Eq. (2),  $\Delta_{ads}F$  is the free energy of adsorption per molecule:  $\Delta_{ads}F = \Delta_{ads}U - T\Delta_{ads}S$ , where  $\Delta_{ads}U$  and  $\Delta_{ads}S$  are the changes in molecular energy and entropy upon adsorption. It is not easy to obtain analytical expressions for  $\Delta_{ads}S$ . In the case of macromolecular polymers,  $\Delta_{ads}S$  is a nontrivial function of  $\phi$ ,  $N$  and  $\theta$ . However,  $\Delta_{ads}U$  is easily found. For macromolecular polymers,  $\Delta_{ads}U = -N\chi_s$  [34], since we are considering athermal chains in the regime where the chains adsorb as trains. Furthermore, we can neglect the  $\phi$  dependence of  $\Delta_{ads}S$  since the monomer concentrations needed to desorb polymers are generally so low that the molecules in

the bulk solution are effectively noninteracting. Hence it follows from Eq. (2) that

$$\ln \phi(\theta) = -N\chi_s + f_0(N, \theta), \quad (3)$$

where  $f_0(N, \theta)$  is some nontrivial function that depends on  $N$  and  $\theta$ . Equation (3) shows that varying  $\chi_s$  results in a shift of the adsorption isotherm along the  $\ln \phi$  axis. The shift of the adsorption isotherm in Fig. 4 is very well predicted by Eq. (3). Furthermore, the shift is proportional to  $N$ , which means that it is very hard to desorb macromolecular polymers of considerable length.

Let us compare this result with the shift of adsorption isotherms for supramolecular polymers. We start from the same Boltzmann equilibrium as in Eq. (2), but now we separate  $\Delta_{ads}F$  into a part that depends on the model parameters and a part that depends solely on  $\theta$ :  $\Delta_{ads}F = \Delta_{ads}F(\{u\}) + \Delta_{ads}F(\theta)$ . Note that here  $\Delta_{ads}F$  is the adsorption energy per monomer. It follows from Eq. (2) that

$$\ln \phi(\theta) = \Delta_{ads}F(\{u\}) + f_0(\theta), \quad (4)$$

where  $f_0(\theta)$  is some nontrivial function that depends on  $\theta$ . The main contribution to  $f_0(\theta)$  is the entropy loss when a monomer is moved from the bulk to the surface region. Analytical expressions for  $f_0(\theta)$  are not available, but again  $\Delta_{ads}F(\{u\})$  is tractable. It is separated according to the three interaction types,  $\Delta_{ads}F(\{u\}) = \Delta_{ads}F(u_{LL}) + \Delta_{ads}F(u_{IS}) + \Delta_{ads}F(u_{bent})$ , and each of these three components can be calculated separately.

Adsorption isotherms of supramolecular polymer adsorption with varying  $\{u\}$  are shown in Fig. 5. For a typical adsorption isotherm as described in Fig. 5—for example,  $u_{LL} = -10$ ,  $u_{IS} = -6$ —the filling of the surface occurs when  $\phi \approx 10^{-6}$ . At this concentration,  $\langle N \rangle \approx 1.09 \approx 1$  according to Eq. (1). This means that the adsorbed monomers at the surface are in equilibrium with a solution that consists almost exclusively of solvent molecules and single monomers. The reaction is therefore associated with the formation of a single *IS* contact. Furthermore, it is very likely that a monomer adsorbs next to a monomer that is already present at the surface, due to the high binding energy. Therefore  $\Delta_{ads}F(u_{LL}) = u_{LL}$  and  $\Delta_{ads}F(u_{IS}) = u_{IS}$ . The shift in Figs. 5(A) and 5(B) are therefore  $\delta = \Delta u_{LL} / \ln 10$  and  $\delta = \Delta u_{IS} / \ln 10$ , respectively. The large prefactor  $N$  in Eq. (3) for macromolecular polymers is missing for supramolecular polymers. We return to this point below.

The quantity  $\Delta_{ads}F(u_{bent})$  is calculated as

$$\Delta_{ads}F(u_{bent}) = -\ln \frac{Q_{surf}^{mon}}{Q_{bulk}^{mon}}, \quad (5)$$

where  $Q_{surf}^{mon}$  and  $Q_{bulk}^{mon}$  are the canonical partition functions of a single monomer at the surface and in the bulk solution. In the present lattice model, a monomer in the bulk is free to position one linking face in any of the  $q$  directions. The other linking face is to be placed on 1 of the  $(q-1)$  remaining directions of which  $(q-2)$  correspond to a bent state [with associated Boltzmann weight  $\exp(-u_{bent})$ ] and only one

corresponds to a linear state. Hence,  $Q_{bulk}^{mon} = q[(q-2)\exp(-u_{bent}) + 1]$ .

For the computation of  $Q_{surf}^{mon}$  we neglect the configurations where one of the linking faces is in contact with the surface. This is reasonable for most situations where  $u_{IS}$  or  $u_{LL}$  is sufficiently negative. It is easily shown that for our model  $Q_{surf}^{mon} = 4[2\exp(-u_{bent}) + 1]$  and hence that

$$\Delta_{ads}F(u_{bent}) = \ln \frac{6[4\exp(-u_{bent}) + 1]}{4[2\exp(-u_{bent}) + 1]}. \quad (6)$$

The shift of the isotherm with varying  $u_{bent}$  is quantified by Eq. (6), as shown in Fig. 5.

For completely flexible chains,  $\exp(-u_{bent}) = 1$ , and for rods,  $\exp(-u_{bent}) = 0$ ; therefore,  $\Delta_{ads}F(u_{bent})$  is at least  $\ln 3/2 \approx 0.405$  (stiff chains) and at most  $\ln 5/2 \approx 0.916$  (completely flexible chains). The entropy penalty of adsorption is less for stiff chains than for flexible chains since stiff chains lose less configurational entropy. This effect is already discussed in detail for semiflexible polymers [35].

In conclusion, we have found that  $\Delta_{ads}F(\{u\})$  can be constructed as follows:

$$\Delta_{ads}F(\{u\}) = u_{LL} + u_{IS} + \ln \frac{6[4\exp(-u_{bent}) + 1]}{4[2\exp(-u_{bent}) + 1]}. \quad (7)$$

Equations (4) and (7) describe the magnitude of a shift  $\Delta \ln \phi$  as a result of a change in  $\{u\}$  quantitatively. We can therefore find any adsorption isotherm in the regime of strong adsorption from a dilute solution if only one is known.

For our present model, the contribution of chain stiffness to  $\Delta F_{ads}$  by increasing the stiffness of the chains is at most  $\ln 5/3 \approx 0.5$ . However, note that nematic ordering of the chains within the plane parallel to the surface is ignored on the present level of approximations. Taking nematic ordering into account would not necessarily lead to accurate results due to lattice artifacts [26]. Therefore the case that the monomers are very stiff may not be accurately described by the present treatment, and from now on we will focus exclusively on completely flexible chains.

The range of validity of Eq. (7) is demonstrated in Fig. 6. Equation (7) is valid when  $\langle N \rangle \approx 1$  at concentrations where filling of the surface occurs. This is the regime where both  $u_{LL}$  and  $u_{IS}$  are sufficiently negative. In this regime, changing the adsorption energy has exactly the same effect on adsorption as changing the linking energy. Since the shape of the adsorption isotherm on a logarithmic  $\phi$  scale is virtually unaffected by a change in either  $u_{LL}$  or  $u_{IS}$ , we can specify the shift of the isotherm by comparing values of  $\phi$  for a given  $\theta$ . This is demonstrated in Fig. 6, for the case  $\theta = 0.5$ , where plot A and plot B of Fig. 6 merge for low  $\Delta F_{ads}$ . Deviations from slope 1 are found when  $u_{LL}$  or  $u_{IS}$  becomes less negative since then the adsorbed layer is not limited to the lattice layer next to the surface. The description given in this section therefore breaks down when the linking energy or the adsorption energy is not strong enough.

At this point, we compare the magnitudes of the shift in the adsorption isotherms for macromolecular polymers (Fig. 4) and supramolecular polymers (Fig. 5). For supramolecular polymers, we find that the isotherm shift associated with a

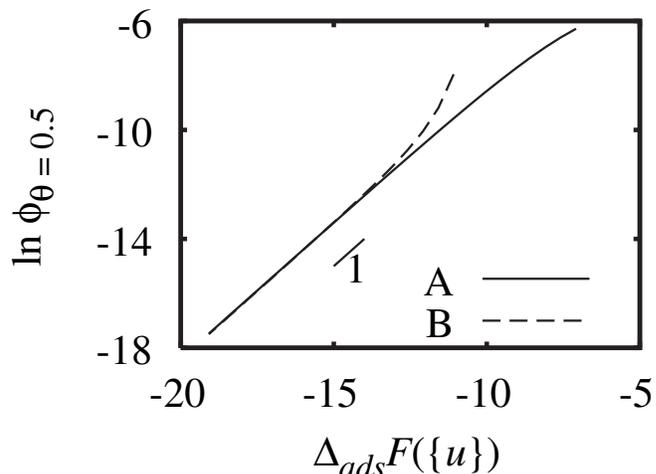


FIG. 6. This plot shows  $\ln \phi_{\theta=0.5}$  versus  $\Delta_{ads}F(\{u\})$  to illustrate the relation between  $\Delta_{ads}F(\{u\})$  and the shift of the adsorption isotherms. The quantity  $\phi_{\theta=0.5}$  is the overall monomer concentration at which  $\theta=0.5$ . Equation (7) with  $u_{bent}=0$  was used to calculate  $\Delta_{ads}F(\{u\})$ . Plot (a): effect of bond energy:  $u_{IS}=-6$ ;  $u_{LL}$  is varied. Plot (b): effect of adsorption energy:  $u_{LL}=-10$ ;  $u_{IS}$  is varied. Equation (4) predicts a slope of unity for this plot.

change of the adsorption energy is in the present regime  $\Delta \ln \phi = \Delta u_{IS}$  whereas for macromolecular polymers,  $\Delta \ln \phi = -N\Delta\chi_s = N\Delta u_{IS}$ . In other words, if the change in adsorption energy per segment is the same, then the isotherms of macromolecular polymers are shifted  $N$  times more than isotherms of supramolecular polymers. Adsorption and desorption of supramolecular polymers occurs within an experimentally accessible concentration window. In the case of macromolecular polymer adsorption, the part of the isotherm where filling of the surface occurs is shifted out of the experimental range due to the large prefactor  $N$ .

## V. COOPERATIVITY OF ADSORPTION

In the previous section, it was shown that the adsorption isotherms of supramolecular polymers are shifted along the  $\ln \phi$  axis as a result of changing the adsorption energy to a much lesser extent than macromolecular polymers. This is necessary but not sufficient for desorption of supramolecular polymers to take place within the experimental range of monomer concentrations. Another requirement is that desorption takes place within a narrow concentration range. Let us arbitrarily define a  $\theta$  interval where filling of the surface occurs,  $0.1 < \theta < 0.9$ , and compare the monomer volume fractions at both ends of this interval. The quotient  $\phi_{\theta=0.9}/\phi_{\theta=0.1}$  is a measure for the range of volume fractions in which the surface is filled. Several values of  $\phi_{\theta=0.9}/\phi_{\theta=0.1}$  for a supramolecular polymer and macromolecular polymers of three chain lengths are given in Table I. In the case of supramolecular polymers, reducing the surface coverage from 0.9 to 0.1 requires reducing the monomer concentration by a factor of about 6. By contrast, for macromolecular polymers of length 100, reducing the surface coverage by the same amount demands a decrease of the concentration by

TABLE I. Values of  $\phi_{\theta=0.9}/\phi_{\theta=0.1}$ , which is a measure of the steepness of the adsorption isotherm, for several types of polymer. Parameters:  $u_{LL}=-10$ ,  $u_{IS}=-4$ ,  $\chi_s=4$ , and  $\chi=0$ .

Polymer		$\phi_{\theta=0.9}/\phi_{\theta=0.1}$
Supramolecular		6.4
Macromolecular	$N=100$	$6.7 \times 10^{95}$
	$N=50$	$2.4 \times 10^{48}$
	$N=10$	$2.6 \times 10^{10}$

almost 100 *decades*. The range reduces with  $N$  but is still 10 decades wide if  $N=10$ , which is very short for polymeric standards.

The physical background of this remarkable difference is cooperativity of adsorption in the case of supramolecular polymers but not in the case of macromolecular polymers. Unlike macromolecular polymers, adsorbing supramolecular chains not only profit from the adsorption energy, but also from favorable interactions with other monomers that are already present at the surface. Since adsorption is enhanced as more monomers adsorb to the surface, it is a *cooperative* process. It would be interesting to try to quantify the degree of cooperativity of polymer adsorption and to compare the degrees of cooperativity for covalent and reversible polymers.

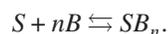
Cooperativity is a widespread notion in quantitative biochemistry and can be quantified by the formalism developed by Hill. The Hill theory was originally formulated to explain the sigmoidal binding curve of oxygen to hemoglobin [36]. This protein has four oxygen-binding sites, but this fact alone is not sufficient to explain the sigmoidal shape of the binding curve. Hill described dissociation of a oxygen-hemoglobin complex by a dissociation constant

$$K_{Hill} = \frac{[P][L]^n}{[PL_n]}, \quad (8)$$

where  $P$  and  $L$  indicate protein and ligand and square brackets denote concentration. Individual protein molecules may differ in the number of bound oxygen molecules. Hence  $n$  in Eq. (8) is in general not an integer.

The parameter  $n$  is known as the Hill coefficient, and it is a measure for the degree of cooperativity of the reaction. If there is no cooperativity,  $n$  is equal to unity. In the case of positive cooperativity,  $n > 1$ , which means that binding is enhanced when more ligands are bound to the protein. On the other hand,  $n < 1$  denotes negative cooperativity.

We use this concept to quantify the degree of cooperativity of polymer adsorption. It is possible to view the adsorption of polymers as an equilibrium reaction between parts of a surface  $S$  and a number of bulk chains indicated by  $B$ :



Here  $S$  is a part of a surface that can accommodate  $B_n$ . The dissociation equilibrium constant of this reaction is

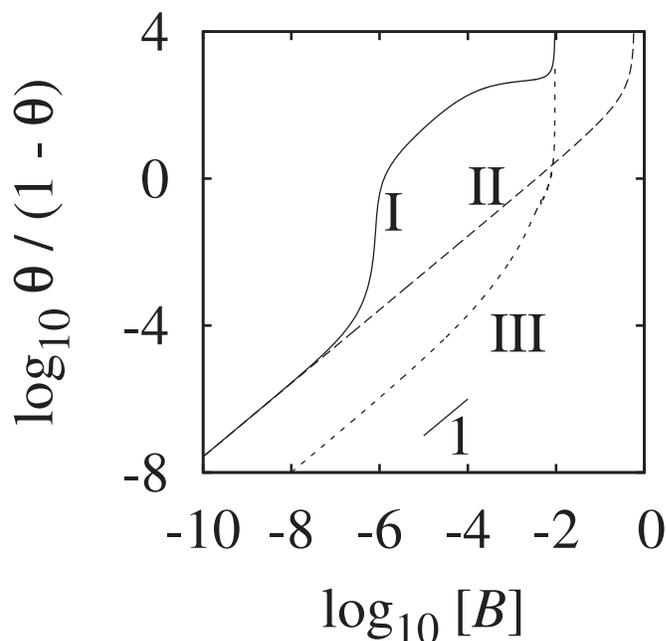


FIG. 7. Hill plots: plot of  $\log_{10}\frac{\theta}{1-\theta}$  versus  $\log_{10}[B]$ , where  $[B]$  is the number concentration of chains. It is inferred from Eq. (11) that the slope of this graph is equal to  $n$ , which is a measure for the degree of cooperativity of the adsorption. Curve I: supramolecular polymers. Parameters:  $u_{IS}=-6$ ,  $u_{LL}=-10$ . Curve II: nonassociating, adsorbing monomers. Parameters:  $u_{IS}=-6$ ,  $u_{LL}=0$ . Curve III: associating monomers without affinity for the surface region. Parameters:  $u_{IS}=0$ ,  $u_{LL}=-10$ .

$$K_d = \frac{[S][B]^n}{[SB_n]}. \quad (9)$$

The Hill coefficient  $n$  is the central parameter to describe cooperativity of polymer adsorption in the present formulation. The quantity  $[B]$  is the number concentration of chains in solution. For macromolecular polymer adsorption,  $[B] = \phi/N$ ; for supramolecular polymers,  $[B] = \phi/\langle N_b \rangle$ , where  $\langle N_b \rangle$  is found by means of Eq. (1).

As in the previous sections, we focus on the case that only trains are adsorbed. We write the saturation of the surface region  $\theta$  as

$$\theta = \frac{[SB_n]}{[SB_n] + [S]} = \frac{[B]^n}{[B]^n + K_d}. \quad (10)$$

We can calculate  $n$  for the supramolecular adsorption by linearizing Eq. (10) according to

$$\log_{10}\frac{\theta}{1-\theta} = n \log_{10}[B] - \log_{10}K_d. \quad (11)$$

The Hill coefficient  $n$  can be found by determining the slope of the plot of  $\log_{10}\theta/(1-\theta)$  against  $\log_{10}[B]$ . Such a plot is known as a *Hill plot*.

Hill plots of supramolecular polymers (curve I) and non-associating (curve II) and nonadsorbing (curve III) monomers are shown in Fig. 7. The adsorption isotherms (not shown) of all three compounds merge when  $\phi \rightarrow 1$  because

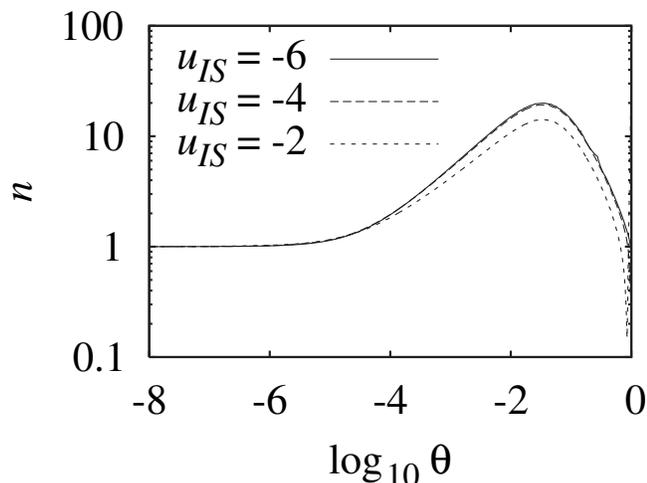


FIG. 8. The slope of the Hill plot, the Hill coefficient  $n$ , is plotted against the logarithm of the surface coverage  $\theta$  for different values of the adsorption energy  $u_{IS}$ . The bond energy was  $-10$ .

the effect of contact energies vanishes in the melt [25]. Curves I and III in Fig. 7 merge at high  $[B]$  because the mean chain length in solution is the same for both monomers. Curves I and II merge at low  $[B]$  because monomers adsorb individually at very low concentrations where  $\langle N \rangle \approx 1$ . We expect to find cooperative adsorption only when both  $u_{LL}$  and  $u_{IS}$  are negative. Indeed, the slopes of curves II and III are unity (except at very high concentrations), which indicates no cooperativity. On the other hand, the region in curve I around  $[B] \approx 10^{-6}$  has a slope much larger than 1, indicating positive cooperativity.

Curve I in Fig. 7 has clearly a nonuniform slope, which means that  $n$  depends on  $\theta$ . This dependence is shown in Figs. 8 and 9. At very low surfaces coverages,  $n$  is equal to unity. This is the Henry regime, where the adsorbed molecules are far apart and do not interact with each other. As  $\theta$  increases,  $n$  exhibits a sharp increase with  $\theta$  (Fig. 9). This indicates that adsorption in this region is strongly enhanced by the presence of other monomers. At a certain point,  $n$

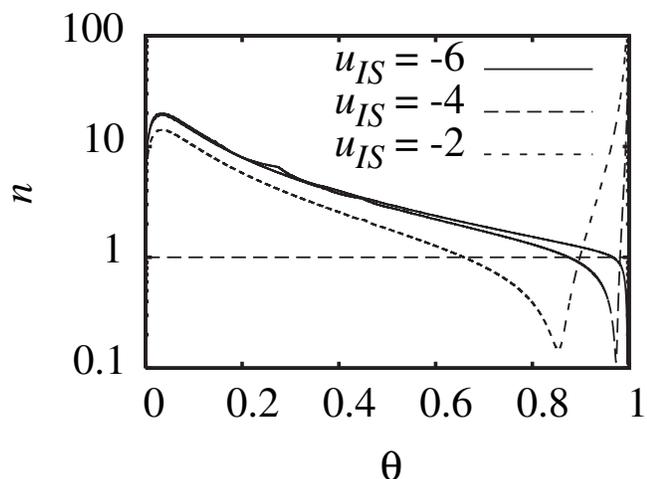


FIG. 9. As in Fig. 8, except  $\theta$  is plotted on a linear scale.

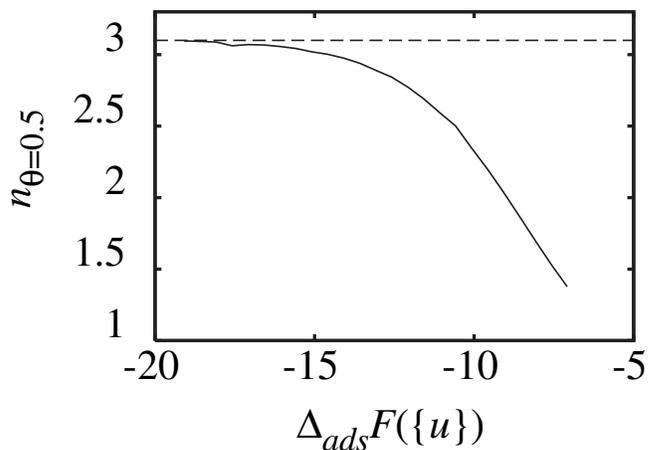


FIG. 10. Dependence of  $n_{\theta=0.5}$  on  $\Delta_{ads}F(\{u\})$ , where  $n_{\theta=0.5}$  is  $n$  at  $\theta=0.5$  and  $\Delta_{ads}F(\{u\})$  is calculated according to Eq. (7). Parameters:  $u_{IS}=-6$ ;  $u_{LL}$  was varied. The maximum value of  $n_{\theta=0.5}$  (shown as a dashed line) can be computed from the adsorption isotherms by means of Eq. (13).

starts to decrease with  $\theta$  because it becomes more difficult to adsorb more monomers due to excluded volume interactions. Still,  $n$  remains larger than unity throughout most of the isotherm where filling of the surface occurs.

It is of interest to assess the effect of  $\Delta_{ads}F(\{u\})$  on the degree of cooperativity. Since  $n$  is strongly dependent on  $\theta$ , it is necessary to compare values of  $n$  at a specific  $\theta$ . We choose arbitrarily to compare values at  $\theta=0.5$ . The plot of  $n_{\theta=0.5}$  versus  $\Delta_{ads}F(\{u\})$  is shown in Fig. 10. Perhaps surprisingly,  $n_{\theta=0.5}$  reaches a plateau for strong adsorption. Apparently, the degree of cooperativity is independent of the strength of adsorption in that region. The origin of this effect can be deduced from an observation made in Sec. IV: namely, that the adsorption isotherms are merely shifted along the  $\ln \phi$  axis at a different  $\Delta_{ads}F(\{u\})$ . The Hill coefficient  $n$  is the slope of the Hill plot; therefore,

$$n = \frac{d \ln[\theta/(1-\theta)]}{d \ln(\phi/\langle N \rangle)}. \quad (12)$$

Since  $\langle N \rangle$  is equal to unity to a very good approximation in this regime, this is equivalent to

$$n = \frac{1}{\theta(1-\theta)} \frac{d\theta}{d \ln \phi}, \quad (13)$$

where the differential quotient on the right-hand side of Eq. (13) is recognized as the slope of the adsorption isotherm plotted on a logarithmic scale. The slope of the adsorption isotherms at a certain  $\theta$  is the same for each value of  $\Delta_{ads}F(\{u\})$ . Therefore  $n$  does not increase indefinitely with decreasing  $\Delta_{ads}F(\{u\})$ .

Summarizing, it was shown that  $n > 1$  for strongly adsorbing supramolecular polymer throughout the (arbitrary) range  $0.1 < \theta < 0.9$ . Let us compare this with macromolecular polymer adsorption. Several Hill plots of macromolecular polymer adsorption are depicted in Fig. 11. These plots are quite similar to adsorption isotherms plotted double

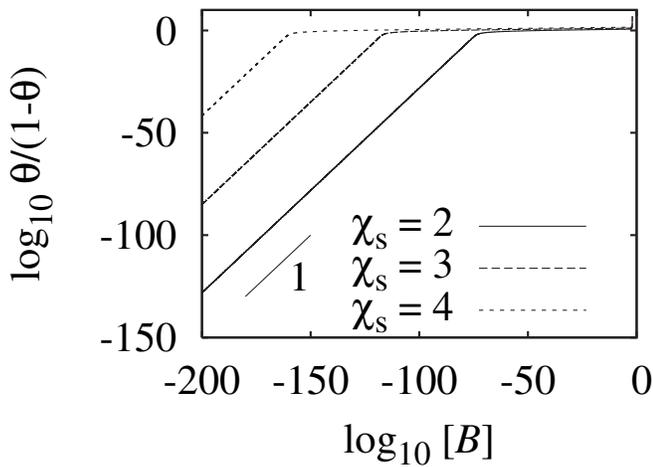


FIG. 11. Hill plots of macromolecular polymer adsorption for different values of  $\chi_s$ .

logarithmically—for example, Ref. [33]. At low concentrations, a Henry regime is observed. At higher concentrations (but still well below the experimental range) a crossover to a pseudoplateau region is found.

The slopes of the Hill plots are shown in Figs. 12 and 13. The plots merge at  $\phi \rightarrow 1$ , since the value of  $\chi_s$  is irrelevant in a polymer melt. Like the Hill plots of supramolecular polymers,  $n=1$  at very low  $\theta$ . However,  $n$  starts to decrease already at a surface coverage of less than 1%, indicating negative cooperativity over the entire range  $0.1 < \theta < 0.9$  for strongly adsorbing polymers. The physical background is obviously excluded volume interactions. In conclusion, a dramatic difference in the cooperativity of adsorption is observed. These results give at least a qualitative explanation for the enormous difference in  $\phi_{\theta=0.9}/\phi_{\theta=0.1}$  between supramolecular polymers and macromolecular polymers.

VI. CONCLUSION

In this paper, a comparison is made between adsorption of supramolecular polymers and macromolecular polymers. It is

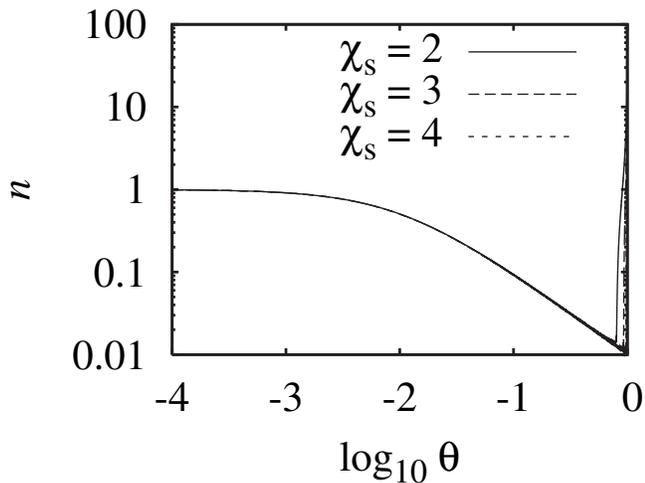


FIG. 12. Dependence of  $n$  on  $\log_{10}\theta$  for macromolecular polymers for different adsorption energies  $\chi_s$ . Parameters: chain length  $N=100$ ,  $\chi=0$ .

found that supramolecular polymers can be desorbed by dilution while this is nearly impossible for high-molecular-weight macromolecular polymers. Two differences between the adsorption isotherms of supramolecular polymers and macromolecular polymers contribute to this discrepancy: in comparison with macromolecular polymer adsorption, adsorption of supramolecular polymers generally occurs at much higher monomer concentrations and within a much narrower concentration range.

We performed numerical calculations to obtain adsorption isotherms of macromolecular and supramolecular polymers in the regime of strong adsorption from dilute solution. Although it is not possible to find an analytical expression for the shape of the isotherms, it is possible to formulate relatively simple expressions for the shift of the isotherm along the  $\ln \phi$  axis as a result of a change in the adsorption energy per segment  $u_{LL}$ . This shift  $\Delta \ln \phi$  is equal to  $\langle N \rangle u_{LL}$ , where  $\langle N \rangle$  is the average number of segments per chain in the surrounding solution. For supramolecular polymers,  $\langle N \rangle$  decreases with decreasing concentration. In the regime that we studied,  $\langle N \rangle \approx 1$  in the part of the isotherm where filling of the surface takes place. By contrast,  $\langle N \rangle$  of macromolecular polymers is generally large and independent of concentration. The shift of the adsorption isotherms by changing  $u_{LL}$  is therefore much more pronounced for macromolecular polymers than for supramolecular polymers. As a result, the part of the isotherm where filling of the surface occurs is beyond the experimental range for macromolecular polymers.

The second important difference between adsorption of macromolecular polymers and supramolecular polymers is the concentration range in which filling of the surface occurs. This takes many decades of concentration in the case of macromolecular polymers, but generally only one decade for supramolecular polymers. This difference is due to the cooperative nature of supramolecular polymer adsorption: up to a certain  $\theta$ , adsorption is enhanced as more monomers adsorb to the surface except at extremely low values of  $\theta$ . The cooperative nature is analyzed by applying the Hill theory to polymer adsorption. The cooperativity parameter is the Hill coefficient  $n$ . If  $n > 1$ , then positive cooperativity is observed and  $n < 1$  in the case of negative cooperativity.

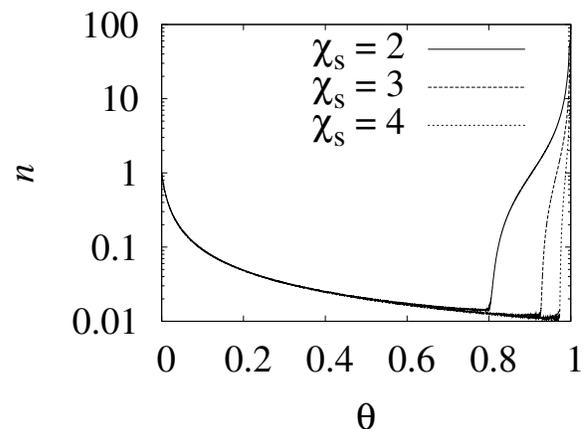


FIG. 13. As in Fig. 12 but now  $\theta$  is plotted on a linear scale.

Polymers adsorb as individual molecules in the Henry regime. Therefore  $n=1$  at very low concentrations both for macromolecular polymers and for supramolecular polymers. For macromolecular polymer adsorption,  $n$  levels off abruptly and enters a pseudoplateau region, which is the regime that is almost exclusively found experimentally. In the case of supramolecular polymer adsorption beyond the Henry regime,  $n$  increases rapidly and a pseudoplateau region is hardly observed in this case. So there is positive cooperativity for supramolecular polymers, but not for macromolecular polymers.

The partition functions of the supramolecular polymer systems were calculated on the quasichemical level of approximation. The partition functions of the macromolecular polymer systems, on the other hand, were obtained by means of the Scheutjens-Fleer theory, which includes excluded volume interactions on the Flory level only. However, the fact that this is a slightly different level of approximation is not relevant at all for the trends presented in this paper. For example, the entropic factors in the equations that describe

the shift of the adsorption isotherms cancel, because all non-local entropic factors are contained in the factors  $f_0(N, \theta)$  and  $f_0(\theta)$  in Eqs. (3) and (4). The magnitude of the shifts upon a variation in  $u_{LL}$  or  $\chi_s$  is therefore completely independent of whether quasichemical or Scheutjens-Fleer calculations were used. Admittedly, there will be small effects on the shape of the isotherms and hence on the data presented in figures of Sec. V. In any case using exactly the same level of approximation would lead to the same conclusions.

Like macromolecular polymers, supramolecular polymers can alter the properties of surfaces and they can switch between flat, hard layers and fluffy, soft adsorbed layers depending on experimental conditions. Unlike macromolecular polymers, however, supramolecular polymers can adsorb and desorb within an experimentally accessible concentration range. Adsorbed supramolecular polymers are therefore more responsive to changes in the monomer concentration. We expect that the results in this paper will therefore increase the appreciation of supramolecular polymers as surface-modifying agents.

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