Modification of Continuum Chain Model of Surface-Interacting Polymers To Describe the Crossover between Weak and Strong Adsorption

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ABSTRACT: Continuum models of flexible polymers give physically incorrect results in situations where polymers are "localized" to restricted regions of space. Limitations of continuum chain theories for confined polymers are illustrated for surface-interacting polymers where both lattice and continuum calculations can be performed *exactly* for ideal chains. This comparison reveals the details of the breakdown of the continuum chain model in the regime of strong polymer adsorption. As a remedy to this difficulty, we formally introduce a corrected continuum chain theory by taking the spatial dimension *d* to depend on the surface interaction in such a way that the lattice and continuum model calculations are required to be consistent for weak and strong polymer adsorption.

1. Introduction

Many theoretical studies of interacting polymers are based on the continuum Wiener path model of flexible polymer chains.[1] There are situations, however, where this continuum chain model breaks down. Difficulties are characteristically found when polymers become "localized" to a restricted region of space, and this class of problems is illustrated by the case of surface-interacting polymers where *exact* continuum and lattice model calculations can be compared for chains without self excluded volume interactions.

Some time ago we noted some physically incorrect behavior[2] of the continuum chain model for strongly interacting polymers while pursuing exact calculations for the properties of end-tethered Gaussian chains interacting with a surface.[3] A comparison of our formally exact calculations for continuum polymer chains with Rubin's corresponding exact calculations for surface-interacting lattice random walks reveals significant discrepancies for certain properties.[3,4] The present paper summarizes (section 2) this comparison, since the difficulties were only briefly mentioned previously.[3] The lessons learned from studying these simple models of surface-interacting polymers should be useful in developing more realistic continuum models of strongly interacting polymers for a variety of applications. A modified version of the continuum surface-interacting polymer model is also introduced which correctly interpolates between the limits of weak and strong polymer adsorption.

2. Surface Interacting Polymers

Numerous theoretical treatments have appeared for polymers interacting with a plane boundary in $d = 3$ dimensions based on both lattice and continuum chain random walk models.[2] Recent studies have been devoted to incorporating excluded volume,[3,5–7] chain stiffness,[8] and other interactions into these surface-inter-acting polymer models. Many of the theoretical treatments are based on the continuum Gaussian chain (Wiener path) model of ideally flexible chains or its field-theoretic equivalent,[1] where the polymer configurations are weighted by a short-range (δ-function) polymer–surface interaction.[2,3,6,7]

Before emphasizing points of disagreement between continuum and lattice models of surface-interacting polymers, it is worth mentioning some common predictions of these models. Let $\langle R_\perp^2 \rangle$ denote the mean-square end-to-end distance of the free end of an end-tethered flexible polymer chain normal to the grafting plane interface, and let $\langle R_\perp^2 \rangle_0$ be the corresponding component of the end-to-end distance of an unconstrained chain in solution. The ratio between these moments defines the chain expansion factor $\gamma_{R_\perp}$,

$$\gamma_{R_\perp} = \langle R_\perp^2 \rangle / \langle R_\perp^2 \rangle_0 \tag{2.1}$$

which approaches 2 for a chain attached to a repulsive interface, 1 for the chain at the "adsorption θ-point", where attractive and repulsive polymer–surface interactions compensate each other, and 0 for strongly adsorbed polymer chains.[4] These values of $\gamma_{R_\perp}$ apply in the limit of long polymer chains ($n \rightarrow \infty$, where n is the number of chain segments). The limiting values for $\gamma_{R_\perp}$ obtained from continuum chain theory[3,5] in the long-chain limit agree with the lattice calculations of $\gamma_{R_\perp}$ by Rubin. Thus, the continuum chain model captures the qualitative feature that attractive polymer surface interactions cause the average chain size to be contracted normal to the plane interface. Continuum and lattice chain calculations also agree on the prediction for the order of the polymer adsorption phase transition.[3,9]

Further comparison between lattice and continuum model calculations reveals significant discrepancies, however. Rubin[4] finds that the projection of the mean-square end-to-end distance $\langle R_\parallel^2 \rangle$ of the end-tethered

chain onto the grafting plane depends on the short-range attractive polymer−surface interaction energy, ϕ_s (units of thermal energy, $k_B T$) of the lattice random walk model,

$$\langle R_{\|}^2 \rangle = (2/3)nl^2\{(3/2)[1 + (1/4)(e^{\phi_s} - 1)^{-1}]^{-1/2}\},$$
$$\phi_s > \phi_\theta, \quad (2.2a)$$

$$= (2/3)nl^2, \qquad\qquad \phi_s < \phi_\theta \quad (2.2b)$$

where ϕ_θ is the value of ϕ_s at the "adsorption θ-point". (This compensation point is the transition point for polymer adsorption in the limit of infinite chain length and is analogous to the θ-point for the polymer self-interaction.) In contrast to these predictions of the lattice model, continuum theory indicates that $\langle R_{\|}^2 \rangle$ equals[3,5−7]

$$\langle R_{\|}^2 \rangle = (2/3)nl^2 \quad \text{(continuum model)} \quad (2.3)$$

which is *independent* of the polymer−surface interaction. The continuum theory incorrectly implies that the adsorbed polymer simply collapses onto the projected "shadow" of the three-dimensional random walk on the two-dimensional surface so that the chain does not "squeeze out" as it is drawn to the surface. Comparison of eqs 2.2 and 2.3 shows that the continuum theory is correct for desorbed chains, i.e. for $\phi_s < \phi_\theta$, and eq 2.3 is still a reasonable approximation for "weakly adsorbed" chains where $\phi_s > \phi_\theta$ and $\phi_s \approx \phi_\theta$. However, when the surface interaction ϕ_s becomes large and the chain's segments are drawn strongly toward the surface, the lattice model calculations yield a *qualitatively different* limiting behavior,

$$\lim_{\phi_s \to \infty} \langle R_{\|}^2 \rangle = nl^2 \qquad (2.4a)$$

from eq 2.3 in the "strong adsorption" limit. The limiting behavior in eq 2.4a is correct for a random walk confined to a plane, while eq 2.3 is incorrect in this limit.

In general, the expansion factor for the in-plane dimensions of long lattice chains is given by,

$$\gamma_{R_{\|}} = \langle R_{\|}^2 \rangle/\langle R_{\|}^2 \rangle_0 = (3/2)[1 + (1/4)(e^{\phi_s} - 1)^{-1}]^{-1/2},$$
$$\phi_s > \phi_\theta \quad (2.4b)$$

$$= 1, \qquad\qquad \phi_s < \phi_\theta$$

and below we also discuss the expansion factor for the chain end-to-end distance,

$$\langle R^2 \rangle = \langle R_\perp^2 \rangle + \langle R_{\|}^2 \rangle$$

$$\gamma_R = \langle R^2 \rangle_{\text{end−tethered}}/\langle R^2 \rangle_0 \qquad (2.5)$$

In summary, when the polymer−surface interaction becomes attractive, the dimensions of the chain projected onto the plane, $\langle R_{\|}^2 \rangle$, and those normal to the plane, $\langle R_\perp^2 \rangle$, are strongly coupled in the lattice model description, while continuum theory predicts a complete *decoupling* of these coordinates.

The discrepancy between the lattice and continuum calculations for γ_R and other properties arises because the "effective dimensionality" d_{eff} in which the chain resides becomes modified by the attractive polymer−surface interactions. A three-dimensional random walk polymer, strongly attracted to a two-dimensional sur-

face, should have the properties of a two-dimensional random walk polymer. In contrast, a weakly adsorbed or desorbed polymer has many loops which extend into the solution, so that it "senses" an effectively three-dimensional space. This physical consideration suggests a modification of the continuum surface-interacting polymer model to describe the variation of the effective dimensionality with the surface interaction and thereby to produce the physically correct limiting behavior of eq 2.4 for strongly adsorbed ideal chains.

The generalization of eq 2.3 to d-dimensional space and to a $d_{\|}$-dimensional surface exhibits the influence of spatial dimensionality on $\langle |R_{\|}|^2 \rangle$ as[3]

$$\langle |R_{\|}|^2 \rangle = (d_{\|}/d)nl^2 \quad \text{(continuum model)} \quad (2.6)$$

Consistency with eq 2.4 requires that d approaches the surface dimension $d_{\|}$ for a strongly attractive surface interaction. Accordingly, we define an "effective dimension" d_{eff} to make eqs 2.3 and 2.6 consistent with the exact lattice result of eq 2.2. This consistency requirement gives

$$d_{\text{eff}} = 2[1 + (1/4)(e^{\phi_s} - 1)^{-1}]^{-1/2}, \quad \phi_s > \phi_\theta, \quad (2.7a)$$

$$= 3, \qquad\qquad \phi_s \leq \phi_\theta,$$

such that we recover the limit,

$$d_{\text{eff}}(\phi_s \to \infty) = 2 \qquad (2.7b)$$

when the embedding space dimension for the non-interacting chain is $d = 3$ and the surface dimension equals $d_{\|} = 2$. (In the diffusion equation describing the continuum model for surface-interacting polymers, the definition of d_{eff} amounts to replacing the "diffusion coefficient" $l/2d$ of the unmodified theory by $l/2d_{\text{eff}}$.) A more general expression is obtained if the random walk calculations are generalized to d-dimensions and the general surface dimensionality $d_{\|}$, but these results are not required here. Replacement of d by d_{eff} in the continuum theory calculations for random walk chains, such as in eq 2.6, then leads to a corrected continuum theory which is now consistent (see below) with its lattice model analog in the strong surface attraction limit, $\phi \gg \phi_\theta$. The consistency condition defining d_{eff} in eq 2.7a is obtained from the infinite chain limit so that the definition (eq 2.7a) must be restricted to long chains. For short chains we can readily calculate the generalization of eq 2.4 to finite chains, which can be equated to eq 2.6 to obtain a d_{eff} parameter dependent on chain length. Our consideration is restricted to long enough chains for the Gaussian chain model to be applicable.

For the concept of "effective dimensionality", d_{eff}, to be meaningful, the definition must also be compatible with chain properties other than $\langle |R_{\|}|^2 \rangle$. For example, the mth moment of the end-to-end distance parallel to the grafting plane is obtained from the corrected continuum theory as[3a]

$$\langle |R_{\|}|^m \rangle = (2\langle R^2 \rangle_0/d_{\text{eff}})^{m/2}\Gamma(1 + m/2) \qquad (2.8)$$

for a two-dimensional surface where d_{eff} replaces d in the standard calculation. It is readily shown that eq 2.8 becomes *exact* both for a strongly attractive surface and for chains which are not adsorbed. The accuracy of eq 2.8 in the case of chains adsorbed with an intermediate degree of attraction and $m \neq 2$, however, requires further examination. The effective surface

approximation (eq 2.8) would be exact if the change in the effective dimensionality amounted to only a change in the statistical segment length. This seems plausible and would be convenient, since random walk chains having short-range correlations certainly have these correlations modified when chains become adsorbed, leading to a modification of the Kuhn length l and further complications than just a change in the effective dimension.[10,11] Exact analytic calculations of the moments $\langle |R_\parallel|^m \rangle$ should be possible in the long-chain limit following the methods of Rubin[4] to provide a test of eq 2.8 for intermediate attractive intractions in the adsorbed chain regime.

At a minimum, the breakdown of the continuum chain theory for strong surface attraction implies that the "universal" scaling variables implied by continuum theory are inadequate to describe adsorbed polymers. Some degree of universality is recovered by the modified continuum model, and this situation is illustrated with the exact continuum model expression for γ_R, defined in eq 2.5, where the effective dimension d_{eff} of eq 2.7 is introduced with the requirement that exact lattice model results are obtained for long chains. Using the standard δ-function polymer–surface interaction pseudopotential in the continuum model gives the dimensionless chain streching factor γ_R of the modified continuum theory as[3]

$$\gamma_R = (2/d_{\text{eff}}) + (1/d_{\text{eff}})\{[\exp(\Delta_s^2)\,\text{erfc}(\Delta_s) + 2\Delta_s/\pi^{1/2} - 1]/\Delta_s^2 Q \quad (2.9a)$$

$$Q = \exp(\Delta_s^2)\,\text{erfc}(\Delta_s), \quad \Delta_s = \pi^{1/2} z_s \quad (2.9b)$$

where z_s is the dimensionless surface interaction given by ($d = 3$, $d_\parallel = 2$)

$$z_s = (3/2\pi)^{1/2} (\beta_s/l) n^{1/2} \quad (2.10)$$

The quantity Q is the ratio of the chain partition function for an end-tethered chain to the partition function of a chain in bulk solution. The polymer–surface interaction parameter β_s vanishes at the "adsorption θ-point" and the surface interaction parameter β_s of the continuum theory can be related to the nearest-neighbor interaction of the lattice model through a matching of properties calculated by these models. An exact calculation of Q for an end-tethered polymer chain (not adsorbed) based on the lattice[12,13] and continuum models[3b] leads to an asymptotic scaling, $Q \sim n^{-1/2} \sim 1/\pi z_s$ for nonadsorbed long chains. Equating these asymptotic results in the large n limit yields a correspondence between lattice and continuum model interaction parameters,

$$\beta_s/l = 3^{-4/3}[1 + 6\,(e^{-\phi_s} - 1)] \equiv 3^{-4/3}\tau \quad (2.11)$$

where the matching is assumed to hold for $\phi_s > \phi_\theta$. The "adsorption θ-point" ($\beta_s = 0$) is defined by the condition

$$\phi_\theta = \ln(6/5) \quad (2.12)$$

which is specific to the cubic lattice and a two-dimensional suface. A plot of the dimensionless interaction parameter τ (proportional to β_s) as a function of ϕ_s, based on the matching procedure above, is shown in Figure 1. The variable τ is chosen for convenience as our reduced temperature parameter. Figure 2 displays d_{eff} as a function of τ, and the expansion factors ($\gamma_{R_\parallel}$,
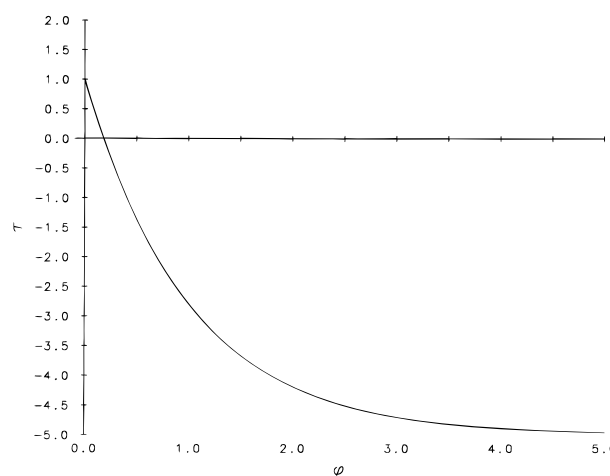

Figure 1. Dimensionless coupling constant τ of the continuum model of polymer adsorption as a function of the nearest-neighbor attractive interaction ϕ_s of the lattice model. Notice that τ saturates at a finite value for large ϕ_s, corresponding to strongly adsorbed chains. In the temperature range above the adsorption θ-point [$\phi_\theta \approx \ln(6/5)$], the surface interaction β_s is reasonably approximated by $\beta_s \approx \beta_s^*[1 - \phi_s/\phi_\theta] = \beta_s^*(T - T_\theta)/T$, $\beta_s^*/l = 3^{-4/3}$. A similar approximation is commonly invoked to describe the short-range polymer–polymer excluded volume interaction.[1]
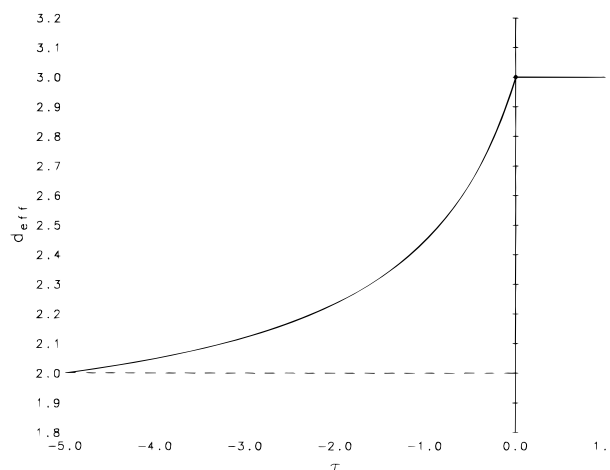

Figure 2. "Effective dimensionality" d_{eff} as a function of the dimensionless polymer–surface interaction τ. The dimensionality equals 3 for the desorbed chain but approaches 2 with an increasing polymer–surface attraction in the adsorbed regime.

$\gamma_{R_\perp}$, and γ_R) calculated from the lattice model are presented in Figure 3 for chains of infinite length. Notably, these functions are not analytic functions of τ.

Having established a relation between lattice and continuum surface interaction parameters, we now consider the crossover expressions for γ_R that emerges from eq 2.9a for finite n. For reference, Figure 4 depicts the "exact" uncorrected continuum result for γ_R with $d_{\text{eff}} = 3$. This calculation produces a simple monotone variation of the chain dimensions γ_R with the surface interaction z_s. Now if d_{eff} is taken to depend on τ as in Figure 2, then the corrected continuum theory produces the rather different crossover expression for γ_R shown in Figure 5. There is a unique scaling curve in the desorbed chain regime ($\beta_s > 0$), but a *family* of scaling functions is found in the adsorbed chain regime ($\beta_s < 0$). The curves exhibited in Figure 5 correspond to fixed values of chain length ($n = 100$, 200, and 300). The chain swelling factor γ_R, according to eq 2.9, can even vary in a nonmonotonic fashion. At first, the chain
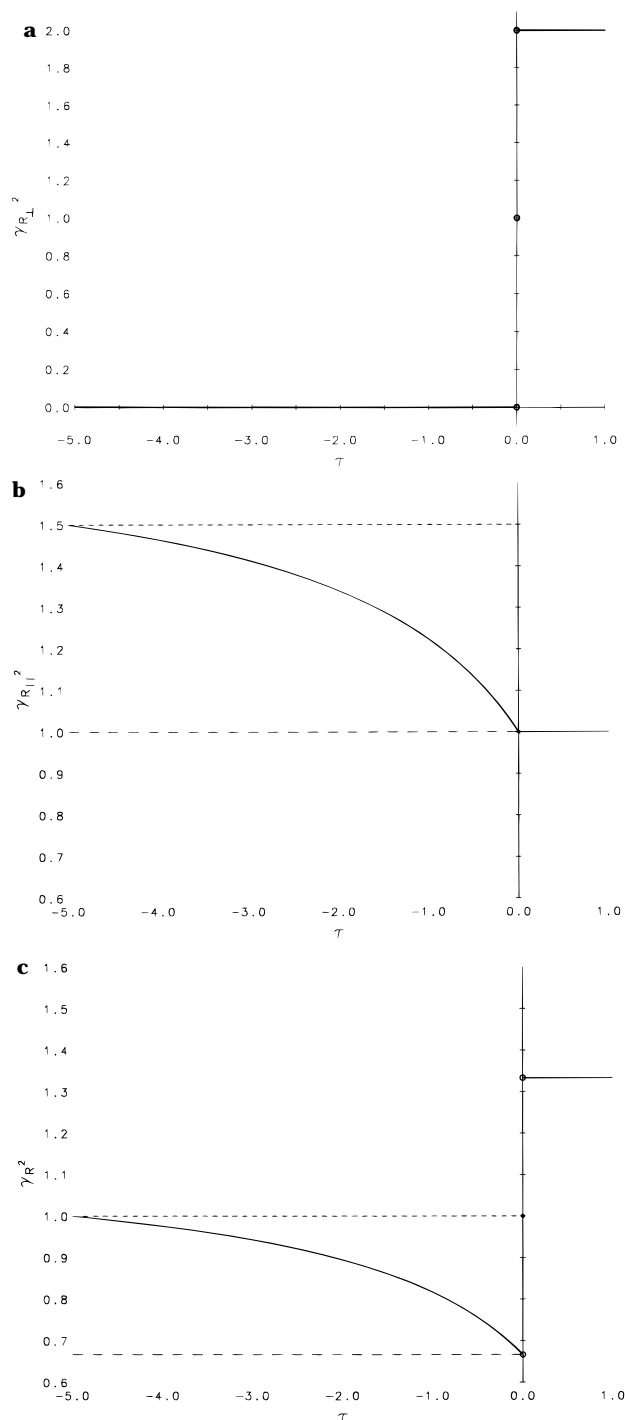
Figure 3. Dimensions of an end-tethered chain relative to those of an unconstrained "free" chain in solution. (a) $\gamma_{R_\perp}$ denotes the mean-square end-to-end distance of the chain component normal to the planar interface relative to the same component of chain size in the absence of the surface. The step-function result for $\gamma_{R_\perp}$ becomes exact in the limit of long chains for both the continuum and lattice chain models. (b) $\gamma_{R_\parallel}$ denotes the mean-square end-to-end distance of the chain position coordinate in the plane of the grafting surface relative to the same component of chain size in the absence of a surface. The chain dimensions within the plane are insensitive to the polymer surface interaction for desorbed chains, while adsorbed chains exhibit a swelling as they are drawn to the surface. The curve is based on the exact lattice model calculations of Rubin[4] in the limit of long chains. The uncorrected continuum chain model calculations yield $\gamma_{R_\parallel}$ as simply equal to unity (dashed curve), independent of the polymer−surface interaction. (c) γ_R denotes the total mean-square dimensions of an end-tethered chain relative to those for an unconstrained "free chain". The curve is exact for lattice chains of infinite length.[4] The dashed line in the adsorbed chain regime ($\tau < 0$) displays uncorrected continuum model calculations.[3]
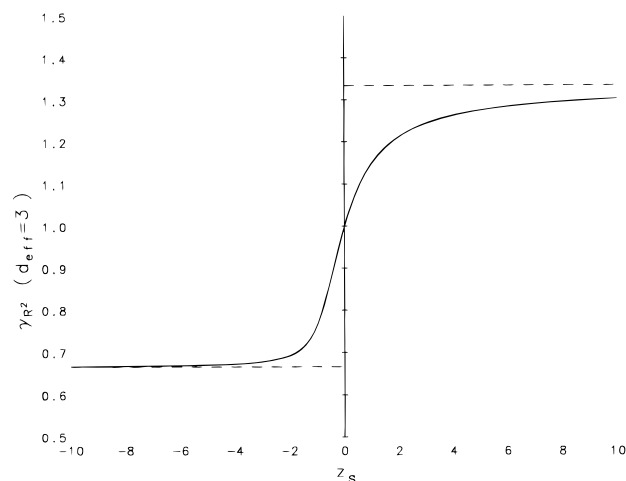
Figure 4. γ_R from the uncorrected continuum chain theory as a function of the dimensionless surface interaction z_s (see ref 3a). The variable z_s of the continuum theory depends on chain length and temperature through the short-range coupling constant β_s (see eq 2.11). Notice the prediction of a universal dependence on z_s and a monotone variation of γ_R with this interaction.
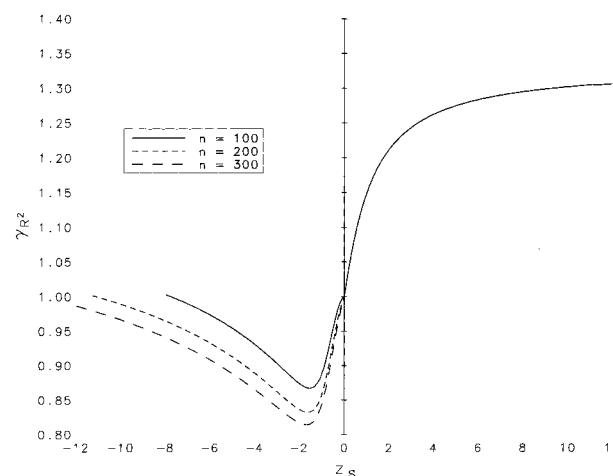
Figure 5. γ_R from the corrected continuum chain model using the concept of an effective dimensionality d_{eff} that depends on the surface interaction. The curves are for $n = 100$ (—), 200 (- - -), and 300 (− − −). Note the nonmonotonic variation of γ_R with z_s.

dimensions tend to decrease as the chain is attracted toward the surface, but the decrease in the effective dimensionality d_{eff} overwhelms this effect, and ultimately the chain swells.

3. Discussion

Although the lattice and continuum models of polymer adsorption agree on many qualitative points, there are important differences between these approaches. Both methods predict that polymer adsorption is accompanied by a decrease of the molecular dimensions of the chain normal to the adsorbing surface.[3,4] Lattice and continuum models also agree on the prediction of the phase transition order.[3,9] However, discrepancies between the lattice and continuum models arise when we examine the dimensions of the adsorbing polymer in the plane of the adsorbing surface. The continuum model predicts that the dimensions of the chain in the plane of the surface are independent of the polymer−surface interaction, while the lattice model predicts that the chain dimensions in the surface expand upon adsorption. This expansion occurs even for unrestricted

random flight chains and becomes more pronounced for chains with short-range correlations.[10,11]

The continuum model of surface-interacting polymers normally represents the surface interaction by a δ-function pseudopotential in the coordinate normal to the surface.[3,6,7] This Gaussian chain model does not account for the coupling between the polymer dimensions normal to the surface and in the plane of the surface, a coupling which is induced by the attractive polymer−surface interaction. Comparisons of exact continuum model calculations[3] with exact lattice model random walk calculations by Rubin[4] for a surface-interacting polymer demonstrate that the continuum chain calculations only provide a physically reasonable description for polymers with *repulsive* polymer−surface interactions and for polymers having weakly attractive surface interactions ("weak adsorption"). When the polymer−surface interaction is strongly attractive ("strong adsorption") and the chains become confined to the surface, the *qualitative* nature of the polymer adsorption in the lattice model differs from that in the continuum theory, which becomes physically incorrect. Through a comparison of lattice and continuum calculations we introduce a corrected version of the continuum theory which reproduces limiting lattice theory results by construction.

Our modification of the continuum chain involves allowing the dimension d of space to be a function of the surface interaction.[14] This modification is physically natural, since the spatial dimension that a polymer "senses" is evidently lower when the chain is strongly adsorbed or otherwise confined.[15] The reduction of dimensionality has a significant influence on chain properties when further interactions are involved, since these interactions usually depend strongly on d. The adsorption transition and similar confinement transitions typically amplify other interactions, such as short-range correlations along the polymer chain and the strength of polymer−polymer excluded volume interactions.[16] There are many other physical models involving confined polymers where the continuum chain theory breaks down and the seriousness of the errors is often larger than that in the polymer adsorption model discussed here. The effective dimension concept should be useful in correcting some of the most serious deficiencies of the continuum chain model for a variety of applications.

References and Notes

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(14) A more general model may at first appear to be provided by a continuum chain model based on a diffusion equation containing two effective dimensionality parameters, $d_{eff,\perp}$ and $d_{eff,\parallel}$, corresponding to motions orthogonal and parallel to the adsorbing plane, respectively. However, a strongly attractive surface quenches the out of plane motion, making $d_{eff,\perp}$ irrelevant. Hence, only a single effective dimension parameter serves to correct the continuum theory.

(15) Similar "dimensional reductions" arise in critical phenomena due to confinement or strong surface interactions. See, for example: Nemirovsky, A. M.; Freed, K. F. *Nucl. Phys. B* **1986**, *270* [FS16], 423. The continuum theory of confined systems breaks down with strong confinement as in the random walk adsorption model, so this model is instructive for a wide range of applications.

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