Polymer–Polymer and Polymer–Surface Excluded Volume Effects in Flexible Polymers Attached to an Interface: Comparison of Renormalization Group Calculations with Monte Carlo and Direct Enumeration Data

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ABSTRACT: The two-parameter model of polymer–polymer excluded volume in conjunction with the renormalization group has recently been generalized to include an interacting plane surface. This system has two types of volume exclusion, the usual polymer–polymer excluded volume interaction and the "excluded volume" constraint of the boundary. A comparison is made between first order in ϵ ($\epsilon = 4 - d$) renormalization group calculations and the results of several Monte Carlo and direct enumeration studies. Special emphasis is given to radial properties such as the end-vector distance $\langle \mathbf{R}^2 \rangle$ and the moments $\langle R_\perp \rangle$ and $\langle R_\perp{}^2 \rangle$ that characterize the average projection of the end-vector distance normal to the plane. Many of these properties have been calculated in previous work, but some new renormalization group calculations are performed for a more complete comparison with Monte Carlo data. Dimensionless combinations of radial properties for a polymer attached to a surface and of the end-vector distance of a free chain are considered in the limit where the magnitudes of the polymer–polymer and polymer–surface interactions are large or vanishing. Dimensionless ratios in these limits should be independent of the details of the underlying lattice or of specific short-range interaction potentials, aside from presumably small contributions arising from ternary interactions. Comparison between the renormalization group theory and lattice data indicates qualitative agreement; however, longer chains must be considered for a quantitative test of the theory.

1. Introduction

Large-scale properties of polymers in the vicinity of an interface are determined by a subtle interplay of polymer–polymer and polymer–surface interactions. There is a competition between the gain of internal energy with the formation of attractive surface contacts and the loss of configurational entropy due to the proximity of the surface.[1] An understanding of these interactions, which can considerably modify polymer properties relative to those of a free polymer chain, is very important for numerous applications in the study of adhesion,[2] stabilization of colloidal dispersions,[3] gel permeation chromatography,[4] and many other areas.[5,6] The mathematical description of this problem is also of intrinsic interest due to its relation to the theory of self-avoiding and random walks in the presence of boundary constraints. Interesting parallels exist between the polymer–polymer and polymer–surface excluded volume interactions.[7] In addition, the theory of a polymer adsorption is closely related to a wide class of phase transition behavior, such a surface magnetism,[8,9] wetting,[10] polymer collapse, the helix–coil transition[11] in biopolymers, etc., which collectively belong to a family of "order–disorder" transitions. Thus, due to practical and purely theoretical reasons, there is considerable interest in developing a precise statistical mechanical theory of surface-interacting polymers.

Models of increasing sophistication have been devised over the past 30 years. Simha et al.[12] give the first serious attempt at a theory of polymer adsorption using a model which neglects the effect of polymer–polymer interaction and which employs "reflecting boundary conditions", so that a random walk encountering the surface is reflected back into solution. The important contribution of this early work is that it established the basic picture of a polymer adsorbed at an interface as a collection of loops extending into solution, trains running along the surface, and tails extending from the end of the polymer to the first surface contact.

A theoretical description of isolated Gaussian chains in the presence of an interacting boundary has been considered by using both lattice random-walk and continuum random-walk models. Rubin[13] provides an extensive study of lattice random walks interacting with a surface for the full range of the surface interaction and calculates many of the important configurational properties of ideal polymers having no polymer–polymer interactions. By using a continuum analogue of the discrete random-walk model, Dolan and Edwards,[3] de Gennes,[14] Chan et al.,[15] and Lêpine and Caillé[16] also make important contributions to the theory of ideal polymers interacting with a surface. The simple random walk–surface interaction model captures many of the qualitative features of surface interacting polymers, but the treatment of the polymer–polymer interaction greatly complicates the problem.

The additional effect of the polymer–polymer interaction has been considered by a variety of methods that yield complementary information. Lattice calculations are especially important because they allow the study of polymer adsorption in a manner where the model parameters can be carefully controlled. Hammersley et al.[17] determine some exact results for the connectivity constant of long self-avoiding walks on lattices. Bounds have been calculated for the critical value of the nearest-neighbor surface interaction at which adsorption occurs for infinite self-avoiding chains.[17-19] Monte Carlo[20-25] and direct enumeration studies[26-28] have been made for numerous configurational properties of self-avoiding walks attached to an impenetrable surface where the reference state is taken to have absorbing boundary conditions[7] such that all configurations that return to the surface are excluded.

Scaling theory provides a powerful heuristic technique of organizing predictions based on simple dimensional analysis in conjunction with reasonable hypotheses or empirical information from lattice chain or real polymer data. de Gennes[8,29] and others[30-32] have applied the scaling theory in conjunction with mean field arguments to discuss a wide range of interesting phenomena associated with the polymer–surface interactions, such as polymer adsorption on surfaces,[29] between plates and in pores,[30,31] and onto colloid particles.[32] Scaling functions cannot directly be calculated with this method but may be deduced indirectly by combining this approach with lattice simulation data.

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Eisenriegler et al.[19] determine semiempirical scaling functions in this fashion for polymers attached to a surface.

The development of analytic theories of surface-interacting polymers has lagged behind the progress made with increasingly sophisticated Monte Carlo simulations[33] and mean field lattice model calculations[34] which consider both the intermolecular and intramolecular excluded volume interactions as well as the polymer–surface interaction. Some early developments of the analytical theory include the self-consistent field calculations of Jones and Richmond[35] to incorporate both polymer–polymer and polymer–surface interactions in the continuum model mean field approximation. Unfortunately, the self-consistent field machinery is very complicated, and only limited results have been produced with this method. Many qualitative results have been obtained by employing generalizations of the mean field lattice calculations in the style of Flory and Huggins. Examples include the work of Silberberg[36] and Hoeve[37] and the more recent work of Scheutjens and Fleer.[34]

The renormalization group (RG) method allows for the systematic resummation of the standard two-parameter (TP) perturbation series of polymer–polymer excluded volume, and it is an important step in the development of a quantitative analytical theory of polymers interacting with a surface. Eisenriegler et al.[19] use a RG method based on the polymer–magnet analogy to discuss the exponents which characterize the asymptotic scaling behavior of chains interacting with a surface. Freed[38] directly employs the *equivalent* TP model and calculates some basic radial properties such as $\langle R^2 \rangle$ and the end-vector distribution function for a polymer at an impenetrable reflecting surface where the polymer–surface interaction vanishes. Eisenriegler[39] calculates some similar properties in this limit and also considers the concentration dependence of polymers near surfaces. Nemirovsky and Freed[40] generalized the TP type approach, which has been traditionally employed in polymer science, to treat the full "double-crossover dependence" on the polymer–polymer and polymer–surface interactions where the polymer–surface interaction is treated *exactly*. The effect of excluded volume and concentration through the semidilute regime can be calculated, in principle, for almost any large-scale property of interest. In this paper we quote some important results of Nemirovsky and Freed[40] for isolated polymers in the proximity of an interacting, impenetrable surface and we provide some new results which are needed in our comparison with Monte Carlo data below. For example, we evaluate the important moment $\langle R_\perp \rangle$ for the average component of the end-vector distance perpendicular to an impenetrable surface. Our primary interest is in checking the consistency of RG predictions for basic configurational properties with available Monte Carlo simulation data for as wide a range of properties as possible before proceeding to the more complicated and practically important concentration-dependent theory.

Polymer adsorption is a topic of very basic significance, and there are many good reviews which consider the topic from different perspectives. Takahashi and Kawaguchi[41] review relevant experiment techniques and the mean field type of approach to polymer adsorption. Whittington,[42] Baumgärtner,[33] and Barber and Ninham[43] review the lattice self-avoiding walk model, while Weiss and Rubin[44] discuss random walks in the presence of barriers. A comprehensive description of polymer and monomer adsorption is given by Dickinson and Lal.[45]

Section 2 describes the extension of the TP model to include a surface interaction. The phenomenological dependence of the model parameters is qualitatively discussed. Basic results for a Gaussian chain interacting with a surface are summarized in section 3, and these are generalized in section 4 to incorporate the polymer–polymer excluded volume. Comparisons are presented in section 5 with Monte Carlo and direct enumeration data, where the relation between boundary conditions for Monte Carlo and continuum theories is also discussed. Section 4 provides a simplified description of the RG theory which stresses general principles rather than technical details. Only a familiarity with the standard TP model is required. As part of our comparison with the Monte Carlo data, it is necessary to identify the adsorption Θ point where the polymer–surface interaction vanishes. New criteria for determining this temperature are proposed in section 5. These criteria are independent of small-scale lattice details and are illustrated with available data. An approximate theoretical expression for the critical adsorption temperature is also obtained. Comparison is made between the properties of a polymer attached to an impenetrable surface and similar properties of a block within an AB diblock copolymer to quantitatively assess the extent of segregation in block copolymers.

2. The Model

The unperturbed model is a continuous Gaussian chain backbone perturbed by δ-function pseudopotentials. Phenomenonlogical parameters in this coarse-grained model are complicated functions of the detailed microscopic interactions. The hypothesis of universality, however, leads us to expect that the microscopic details can be described in terms of the scaling variables derived from a minimal model, so that we expect to obtain a universal description of large-scale properties. Arguments based on the scaling and Mayer cluster theory[46,47] indicate that this type of universal description of long flexible chains with short-range excluded volume interactions is only to be expected in the limit of very long chains. Correction terms associated with the finite chain length for the polymer–polymer interaction are described elsewhere,[47,48] and similar contributions should arise in the case of the polymer–surface interaction. We confine attention to polymer chains that are sufficiently long to be reasonably well described by an idealized Gaussian under Θ conditions, where the *effective* polymer–polymer binary interaction vanishes.[47,48]

The continuous chain model configuration is specified by the position vector $R(x)$ of the chain segment at a contour distance x along a chain of unit length N_0. For convenience, the position vector $\mathbf{R}(x)$ is written in terms of reduced units of the mean square end-to-end distance $\langle \mathbf{R}^2 \rangle_{0,f}$ of a free unperturbed chain

$$\mathbf{r}(x) = \mathbf{R}(x)[d/\langle \mathbf{R}^2 \rangle_{0,f}]^{1/2} \tag{2.1}$$

with d the dimensionality of space in which the polymer is imbedded. The dimensionless configurational Hamiltonian for polymer–polymer interactions and the polymer–surface interactions is then

$$\mathcal{H}/k_B T = \mathcal{H}_0 + \mathcal{H}_I(\text{polymer–polymer}) + \mathcal{H}_s(\text{polymer–surface}) \tag{2.2}$$

where the unperturbed portion

$$\mathcal{H}_0 = (1/2)\int_0^1 dx\, |d\mathbf{r}(x)/dx|^2 \tag{2.2a}$$

reflects chain connectivity. The polymer–polymer interaction for general m-body interaction equals[48]

$$\mathcal{H}_I = \sum_{m=2}^{\infty} (z_m^0/m!) \int_0^1 dx_1 \dots \int_0^1 dx_m \, (2\pi)^{(m-1)(d/2)} \prod_{k=1}^{m-1} \delta[\mathbf{r}(x_k) - \mathbf{r}(x_{k+1})] \quad (2.2b)$$

$$|x_{k+1} - x_k| \leq a/N_0$$

where a/N_0 is a cut-off introduced to exclude contributions from unphysical self-intersections of the chain. The m-body dimensionless interaction parameters are written as[48]

$$z_m^0 = (d/2\pi l^2)^{d(m-1)/2} \beta_m^0 n_0^{\phi_m}, \qquad \phi_m = m - (m-1)(d/2) \quad (2.2c)$$

where l is the Kuhn length and β_m^0 is the usual m-body cluster integral. The number of statistical segments n_0 is related to the free chain end-vector distance $\langle \mathbf{R}^2 \rangle_{0,f}$ through the definition $\langle \mathbf{R}^2 \rangle_{0,f} = n_0 l^2$. Short-range correlations, such as the constraint against immediate reversal in lattice chains and restrictions on bond angles in real polymers, are implicitly absorbed into the definition of l. Restricting (2.2c) to $m = 2$ and $m = 3$ reduces the polymer–polymer interaction model to the three-parameter theory of Yamakawa.[49]

The interacting surface is a hypersurface of dimension $d_\parallel$ and is embedded in a space of dimensionality d. A vector $\mathbf{r}_\parallel(x)$ is defined as the projection of $\mathbf{r}(x)$ onto this surface, and the projection onto an orthogonal surface of dimension $d_\perp$ ($d = d_\perp + d_\parallel$) is written as $\mathbf{r}_\perp(x)$. Our model of the binary polymer–surface interaction is similar to the binary polymer–polymer excluded volume interaction given in (2.2) and is[40,50]

$$\mathcal{H}_s(\text{binary polymer–surface}) = z_s^0 \int_0^1 dx \; \delta^{d_\perp}[\mathbf{r}_\perp(x)](2\pi)^{d_\perp/2} \quad (2.2d)$$

where the binary polymer–surface interaction z_s^0 is defined as

$$z_s^0 = (d/2\pi l^2)^{d_\perp/2} \beta_s^0 n_0^{\epsilon_\perp/2}; \qquad \epsilon_\perp = 2 - d_\perp \quad (2.2e)$$

and where β_s^0 is the polymer–surface binary cluster integral. The $d_\perp$ superscript of the δ function indicates that its argument is a $d_\perp$-dimensional vector. More generally, there are m-body polymer–surface interactions[51] ($m > 2$) but these are marginal ($m = 3$) or irrelevant ($m \geq 4$) in $d = 3$. For strongly adsorbed polymers, however, there is a "dimensional reduction" from d to $d_\parallel$ dimensions, so that excluded volume effects become stronger. If $d = 3$ and $d_\parallel = 2$, then the entire countable infinities of z_m^0 and $z_{s,m}^0$ interactions[51] are, in principle, relevant in the adsorbed state ($d = 2$), reflecting the high density of a strongly adsorbed polymer.[48] As a consequence we follow de Gennes[14] and confine attention to "weakly adsorbed" polymers and to polymers with a repulsive surface interaction.

The influence of polymer–polymer and polymer–surface ternary interactions should be generally small in the $d = 3$ unadsorbed state, and estimates are given in ref 47 for z_3^0 based upon free-chain experimental data and Monte Carlo simulation data. At the compensation points, where the effective binary polymer–polymer or the polymer–surface interactions vanish, these ternary effects may not entirely be negligible for some polymer properties. Previous analysis with free chains shows that the influence of ternary effects, however, can be neglected[48] when considering *ratios* of related properties relative to the Θ reference state, a procedure eliminating a large measure of the ternary effects. Interpretation of the binary interaction model is restricted to these reduced ratios, and the considerations regarding the relevance of ternary surface interactions[51] are the same as those for the polymer–polymer ternary interactions described in ref 47 and 48 for free chains.

The qualitative phenomenological dependence of β_s^0 and β_2^0 can be deduced from a coarse-grained model of the local potential of the mean binary interaction. A minimal description of the van der Waals interaction accounts for the fact that the interaction is dominated by a repulsive short-range hard core with a longer range attractive interaction. A simple model of β_s^0 and β_2^0 is provided by square-well potentials with hard core radii σ_s and σ_2, ranges of attraction Λ_s and Λ_2 in units of σ_s and σ_2, respectively, and attractive potential well depths φ_s and φ_2 in the energy units $k_B T$. The theory of nonideal gases yields for these square-well potentials[50,52]

$$\beta_2^0/l^d \propto (\sigma_2/l)^d[1 - (\Lambda_2^d - 1)(e^{\varphi_2} - 1)] \quad (2.3a)$$

$$\beta_s^0/l^{d_\perp} \propto (\sigma_s/l)^{d_\perp}[1 - (\Lambda_s^{d_\perp} - 1)(e^{\varphi_s} - 1)] \quad (2.4a)$$

The values of φ_s and φ_2 which make β_s^0 and β_2^0 vanish, respectively, are denoted $\varphi_s^{\Theta_A}$ and $\varphi_2^{\Theta_F}$. A similar dependence for β_2^0 is found in the lattice self-avoiding walk model with nearest-neighbor interactions,[53,54] where the potential range term $(\Lambda_2^d - 1)$ is replaced by a term involving the coordination number of the lattice. Equations 2.3a and 2.4a, however, do not take into account the effects of chain connectivity and ternary interactions, which have an influence in determining the observed *effective* binary interaction. Elsewhere[55] we will discuss how these contributions modify (2.3a). Equations 2.3a and 2.4a should then not be interpreted too literally except in the limit of large dimension or coordination number, where the connectivity effect becomes less important.

The idealized interaction parameters φ_2 and φ_s in the square-well and lattice models obviously reflect highly coarse-grained models of the true complicated polymer, surface, and solvent interactions in real polymer–solvent–surface systems and cannot be given a literal microscopic interpretation. For the limit of a shallow attractive interaction ($\varphi_2, \varphi_s \ll 1$) (2.3a) and (2.4b) reduce to the standard forms[14,56]

$$\beta_2^0 \propto (\sigma_2/l)^d[1 - \Theta_F/T] + \mathcal{O}(\varphi_2^2); \qquad \Theta_F = (\Lambda_2^d - 1)/k_B \quad (2.3b)$$

$$\beta_s^0 \propto (\sigma_s/l)^{d_\perp}[1 - \Theta_A/T] + \mathcal{O}(\varphi_s^2); \qquad \Theta_A = (\Lambda_s^{d_\perp} - 1)/k_B \quad (2.4b)$$

Despite the crudeness of this argument, the dependences[19,57,58] (2.3b) and (2.4b) on temperature are found to be good approximations [$\varphi_2 \in (0, \varphi_2^{\Theta_F})$] for lattice polymers for $\beta_2^0, \beta_s^0 > 0$ when $(\sigma_2/l)^d$, $(\sigma_s/l)^{d_\perp}$, Θ_F, and Θ_A are taken as purely phenomenological parameters that are strongly dependent on the particular lattice considered. There is also evidence that (2.3b) holds for an empirical analogue of β_2^0 over a wide temperature[56,60] range for many real polymers in solution where the lower critical solution temperature is much higher than the Θ temperature. However, the lattice simulations of Eisenriegler et al.[19] demonstrate that the value of Θ_A depends on the polymer–polymer interaction, and we must anticipate that the polymer–surface interaction is dependent on the polymer–polymer interaction. It is also possible that the polymer–surface interaction affects the Flory Θ point Θ_F for the polymer–polymer interaction when chains are near the surface, so that the variation of the phenomenological counterparts of β_2^0 and β_s^0 is expected to be more complicated than in the case of a single interaction. These effects deserve to be more carefully studied in Monte Carlo

simulations and eventually in real polymer–surface systems.

A better understanding of the dependence of model parameters would be very useful because completely unambiguous tests between Monte Carlo calculations and the renormalization group theory could then be made over the full crossover range from self-avoiding to Θ chains and from absorbing to reflecting boundary conditions. In this work attention is primarily confined to the Θ point and high-temperature limits for universal ratios of long chains where there is insensitivity to these lattice details.

3. Gaussian Chain Interacting with a Surface

The statistical mechanics of long flexible Gaussian polymer chains interacting with surfaces has been studied extensively in both lattice and continuum theories.[12-15] Most of the qualitative features of polymer adsorption are described by this interesting reference theory.

An extension of the TP perturbation theory to include a surface binary interaction proceeds by first expanding about a suitable reference state and then by employing the renormalization group to resum the resulting perturbation expansion to obtain a theory valid over a wide range of polymer–polymer interaction. Earlier renormalization group calculations by Kosmas[50] employ a double expansion in z_s^0 and z_2^0. However, the perturbative expansions in z_s^0 is *not necessary*. Nemirovsky and Freed[40] utilize as their reference state the Gaussian state theory already perturbed by the surface interaction. *Only an expansion in z_2^0 is required* since the *full* surface interaction z_s^0 dependence is retained from the outset. The reference state is defined by the canonical partition function[40] $Q(\Delta_0)$

$$Q(\Delta_0) = \int \mathcal{D}[\mathbf{r}(x)] \exp\{-\mathcal{H}^0(\Delta_0)/k_BT\} \quad (3.1)$$

$$\mathcal{H}^0(\Delta_0)/k_BT = (\mathcal{H}_0 + \mathcal{H}_s)/k_BT = (1/2)\int_0^1 dx \left|\frac{d\mathbf{r}(x)}{dx}\right|^2 + 2^{1/2}\Delta_0 \int_0^1 dx\, \delta[r_\perp(x)] \quad (3.1a)$$

where $\mathcal{D}[\mathbf{r}(x)]$ is the conformational measure. The variable z_s^0 (see section 2) restricted to $d_\perp = 1$ is denoted by $z_s^0(d=3) = \Delta_0/\pi^{1/2}$, in conformity with the notation of Nemirovsky and Freed.[40] The general variable z_s^0 is used in reference to the perturbative surface interaction model of Kosmas[50] where $d_\perp$ is *not* a fixed paramter. When the surfaces are impenetrable, the integrations in (3.1) are restricted to those polymer configurations confined to the positive half-space with $r_\perp(x) \geq 0$. The Hamiltonian $\mathcal{H}^0(\Delta_0)$ contains the usual $\mathcal{H}_0$ contribution of the full-space theory and a surface portion that can be specified alternatively by providing the boundary conditions satisfied by polymer distribution functions on the surface. The model of (3.1) has $d_\perp = 1$ and $d_\parallel = d - d_\perp$. Kosmas's approach,[50] on the other hand, chooses $d_\parallel = 2$ and $d_\perp = 2 - \epsilon$ so that the theory involves a *single* ϵ-perturbative parameter (see section 2) when polymer–polymer excluded volume is incorporated into the theory. The availability of two different approaches which are equivalent for $d = 3$ is useful when polymer–polymer interactions are introduced and approximations become a necessity. Here we focus solely on the $d_\perp = 1$ model, while both approaches will be compared in a forthcoming paper.

A. Distribution Functions and Boundary Conditions. The fixed end-vector partition function $G^0(\mathbf{r},\mathbf{r}^*,\Delta_0)$ is defined in terms of the Hamiltonian $\mathcal{H}^0(\Delta_0)$ of (3.1) as

$$G^0(\mathbf{r},\mathbf{r}^*,\Delta_0) = \int_{\mathbf{r}(0)=\mathbf{r}^*}^{\mathbf{r}(1)=\mathbf{r}} \mathcal{D}[\mathbf{r}(x)] \exp\{-\mathcal{H}^0(\Delta_0)/k_BT\} \quad (3.2)$$

and it satisfies the usual diffusion equation

$$\left(\frac{\partial}{\partial n_0} - \frac{1}{n_0}\frac{\nabla_r^2}{2}\right) G^0(\mathbf{r},\mathbf{r}^*,\Delta_0) = \delta(\mathbf{r}-\mathbf{r}^*)\delta(n_0) \quad (3.3)$$

supplemented by the boundary conditions

$$\lim_{r_\perp \to 0^+} \frac{1}{G_\perp^0}\frac{\partial}{\partial r_\perp} G_\perp^0 = 2^{1/2}\Delta_0 \quad (3.3a)$$

and

$$G_\perp^0 \to 0 \quad (3.3b)$$

as $r_\perp$ or $r_\perp^* \to \infty$ with $|r_\perp - r_\perp^*| \to \infty$ and for $r_\perp$ or $r_\perp^* < 0$. In the absence of boundaries, the free-chain Green's function $G^0(\mathbf{r},\mathbf{r}^*)$ is translationally invariant. Because of the indistinguishability of the chain ends the Green's functions with surface interactions are symmetric functions of their arguments $G^0(\mathbf{r},\mathbf{r}^*) = G^0(\mathbf{r}^*,\mathbf{r})$, but the presence of the surface breaks the translational invariance of the full space, so that $G^0(\mathbf{r},\mathbf{r}^*) \neq G^0(|\mathbf{r}-\mathbf{r}^*|)$.

The boundary conditions in (3.3) are discussed by de Gennes,[14] but it is worthwhile to review their physical interpretation. If $\Delta_0 = 0$, eq 3.3a reduces to the Neumann boundary condition, which is utilized by Freed[38] and by Eisenriegler[39] for a reflecting wall where the flux of polymer through the wall vanishes. Attractive ($\Delta_0 < 0$) and repulsive ($\Delta_0 > 0$) interfaces make the wall act, respectively, as a sink and as a source of monomers, corresponding to an excess or deficiency of polymer near the surface. An impenetrable repulsive wall has $\Delta_0 \gg 1$, and (3.3a) tends in this case toward the Dirichlet boundary conditions where G^0 vanishes on the surface (because monomers are strongly repelled by the surface). An impenetrable attractive wall arises when $\Delta_0 << -1$, and the chain originally embedded in a d-dimensional space collapses to the $d-1$ dimensional surface as discussed below.

Monte Carlo[20-25] simulations introduce boundary conditions in a somewhat different fashion. They begin, following DiMarzio,[7] with the ensemble of chains in full space. Absorbing boundary conditions at a surface are introduced to remove those unwanted chain configurations that cross to $r_\perp < 0$. The continuum approach, on the other hand, starts from an ensemble of chains *already confined to* $r_\perp \geq 0$. The Monte Carlo absorbing boundary conditions correspond to $\Delta_0 \to \infty$. Lattice Monte Carlo calculations also introduce an attractive polymer–surface interaction for polymer segments that are nearest neighbors to the surface. A sufficiently large value of this parameter corresponds in the continuum theory to a compensation point where $\Delta_0 \to 0$, and then the distribution functions approach those of reflecting boundary conditions. Of course, polymer–polymer interactions can be appended in both approaches as is done for full space polymers.

B. End-Vector Distribution for an Impenetrable Surface. Lépine and Caillé[16] derive the unnormalized end-vector distribution G^0 for an impenetrable interface in the absence of excluded volume. We summarize some of their results (generalized to d dimensions) since the Gaussian theory with full polymer–surface interaction provides our reference state for perturbative calculations in the usual z_2^0 excluded volume parameter. The unnormalized end-vector distribution $G^0(\mathbf{r},\mathbf{r}^*,\Delta_0)$ factors into parallel $G_\parallel^0$ and perpendicular $G_\perp^0$ distributions as[16,40]

$$G^0(\mathbf{r},\mathbf{r}^*,\Delta_0) = G_\parallel^0(\mathbf{r}_\parallel - \mathbf{r}_\parallel^*,\Delta_0) G_\perp^0(r_\perp, r_\perp^*,\Delta_0) \quad (3.4a)$$

(The factorization (3.4a), however, does not hold in the presence of the excluded volume interaction.) $G_\parallel^0$ is unaffected by the interaction with the surface as may be anticipated on physical grounds, so $G_\parallel^0$ is a Gaussian distribution in $d_\parallel = d - 1$ dimensions. The translational

invariance of the full space theory is broken along the $r_\perp$ direction, and $G_\perp{}^0$ is given by[16,40]

$$G_\perp{}^0 = (2\pi)^{-1/2}\{\exp[-(r_\perp - r_\perp{}^*)^2/2] + \exp[-(r_\perp + r_\perp{}^*)^2/2]\} - (4\pi)^{1/2}\Delta_0 \exp[\Delta_0{}^2 + 2\Delta_0(r_\perp + r_\perp{}^*)/2^{1/2}] \operatorname{erfc}[\Delta_0 + 2^{-1/2}(r_\perp + r_\perp{}^*)] \quad (3.4b)$$

where erfc is the error function complement.

A "tail" chain has $r_\perp{}^* = 0$ and $r_\perp \neq 0$. Then, the leading contribution to (3.4b) in the $\Delta_0 \to \infty$ limit of a strongly repulsive interface vanishes and $G_\perp{}^0$ becomes

$$G_\perp{}^0(r_\perp,0;\Delta_0\to\infty) \propto \exp[-r_\perp{}^2/2] r_\perp \Delta_0{}^{-1} + \mathcal{O}(\Delta_0{}^{-2}) \quad (3.5a)$$

When both ends are anchored to the wall, the chain forms a loop, whereupon (3.4b) in the $\Delta_0 \to \infty$ limit yields

$$G_\perp{}^0(r_\perp = r_\perp{}^* = 0, \Delta_0 \to \infty) \propto \Delta_0{}^{-2} + \mathcal{O}(\Delta_0{}^{-3}) \quad (3.5b)$$

The $\Delta_0 \to -\infty$ limit of a highly attractive surface reduces the distribution $G_\perp{}^0$ of (3.4b) to

$$G_\perp{}^0(r_\perp, r_\perp{}^*; \Delta_0 \to -\infty) \propto |\Delta_0| \exp\{\Delta_0{}^2 - 2^{1/2}\Delta_0(r_\perp + r_\perp{}^*)\}[1 + \mathcal{O}(\Delta_0{}^{-1})] \quad (3.5c)$$

The end-vector distribution $G_\perp$ of (3.5c) decays exponentially when either end departs from the wall. As $\Delta_0 \to -\infty$, no end is allowed to escape from the $d_\parallel = d - 1$ hypersurface, and the full chain is embedded in a $(d - 1)$-dimensional space.

C. Some Selected Properties of a Gaussian Chain Interacting with a Surface. Our comparison with Monte Carlo data in section 4 is primarily concerned with the averages $\langle R_\perp{}^m \rangle$ and $\langle R_\parallel{}^m \rangle$, which characterize the average projection of the end-vector distance perpendicular and parallel to the interacting plane. These properties can be calculated exactly for Gaussian chains with a variable surface interaction, and they provide an important reference point when proceeding to the more general case of both variable polymer–polymer and polymer–surface interactions. We now summarize some basic results required below in our comparison of theory with Monte Carlo data.

The mth moment $\langle R_{\parallel,\perp}{}^m \rangle$ of the distribution G^0 for tail chains with $r_\perp{}^* = 0$ is defined by

$$\langle R_{\parallel,\perp}{}^m \rangle_0 = \int d^d\mathbf{R} |R_{\parallel,\perp}|^m G^0(\mathbf{r},\mathbf{r}^*=0;\Delta_0) / \int d^d\mathbf{R} G^0(\mathbf{r},\mathbf{r}^*=0;\Delta_0) \quad (3.6)$$

These moments can be evaluated with (3.4) in closed form and are given in ref 40 for general Δ_0. Since $G_\parallel{}^0$ is the usual $d - 1$ dimensional Gaussian distribution, the $\langle R_\parallel{}^m \rangle_0$ are identical with their $d - 1$ dimensional full space values. Now we quote $\langle R_\perp{}^m \rangle_0$ in the interesting limits of $\Delta_0 \to \infty$ and $\Delta_0 = 0$, relevant for our comparison with Monte Carlo results

$$\langle R_\perp{}^m \rangle_0 = [2\langle \mathbf{R}^2 \rangle_{0,f}/d]^{m/2}\Gamma[(m+1)/2]\pi^{-1/2}, \qquad \Delta_0 \to 0 \quad (3.7a)$$

$$\langle R_\perp{}^m \rangle_0 = [2\langle \mathbf{R}^2 \rangle_{0,f}/d]^{m/2}\Gamma[(m+2)/2], \qquad \Delta_0 \to \infty \quad (3.7b)$$

These limiting cases are very simply calculated from (3.4b) since for $r_\perp{}^* = 0$ and $\Delta_0 = 0$ (3.4b) is proportional to $G_{\perp,f}{}^0$ for a free chain and for $\Delta_0 \to \infty$ (3.4a) becomes proportional to $r_\perp G_{\perp,f}{}^0$ as indicated in (3.5a). Equation 3.7 and the discussion above yield the useful dimensionless ratios

$$\langle R_\perp{}^m(\Delta_0\to\infty)\rangle_0 / \langle R_\perp{}^m(\Delta_0=0)\rangle_0 = \pi^{1/2}\Gamma[(m+2)/2]/\Gamma[(m+1)/2], \qquad m = 1, 2, \ldots \quad (3.8a)$$

and for large m

$$\langle R_\perp{}^m(\Delta_0\to\infty)\rangle_0 / \langle R_\perp{}^m(\Delta_0=0)\rangle_0 \sim (m\pi/2)^{1/2} \quad (3.8b)$$

The following section discusses how the addition of the excluded volume interaction alters these results.

4. Polymer–Polymer and Polymer–Surface Excluded Volume Interactions

Nemirovsky and Freed[40] calculate a variety of properties for a polymer interacting with a plane surface where the surface interaction is treated exactly and where the TP model is used in conjunction with the RG method. Before summarizing the required results along with some new renormalization group calculations based upon the same model and before comparing with Monte Carlo and direct enumeration data, it is instructive to schematically review these RG calculations.

A. Perturbation Expansions and Results of RG Theory. Expanding the polymer–polymer interaction $\mathcal{H}_I$ (polymer–polymer) in (3.2) gives

$$G(\mathbf{r},\mathbf{r}^*;\Delta_0,z_2{}^0) = G^0(\mathbf{r},\mathbf{r}^*;\Delta_0) - z_2{}^0 \int_0^1 dx \int_0^x dx' \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';1-x;\Delta_0) G^0(\mathbf{r}',\mathbf{r}';x-x';\Delta_0) G^0(\mathbf{r}',\mathbf{r}^*;x';\Delta_0)(2\pi)^{d/2} + \mathcal{O}[(z_2{}^0)^2] \quad (4.1)$$

independent of the particular geometry or surface interaction. The fixed end-vector partition function G^0 is obtained by solving the diffusion equation (3.3) subject to the boundary conditions associated with the confining geometry. The only apparent constraint against the direct application of the TP model with $z_2{}^0 \neq 0$ for an arbitrary geometries is that the dimensions of the confining region must be larger than the mean polymer radius of the free chain.[61] There are evidently numerous geometries, branching types, and polymer properties that can be considered based on this formalism. The main difficulty of these calculations is that the algebra becomes increasingly complicated as we proceed to more complex geometries and branching types.

The RG theory calculations, based upon the expansion (4.1) proceed in the same fashion as for the free chain. Thus, any radial property P, such as the mean square end-vector distance $\langle \mathbf{R}^2 \rangle$ for a polymer attached to a surface, is evaluated as a formal Taylor expansion in $z_2{}^0$. Polymer properties P scaling as a radius to the pth power in the usual TP type perturbation expansion have the general form

$$P = G_P \langle \mathbf{R}^2 \rangle_{0,f}^{p/2} \alpha_P^p(z_2{}^0) \quad (4.2)$$

where G_P is a Δ_0-dependent prefactor calculated for Gaussian chains and the expansion factor $\alpha_P^p(z_2{}^0)$ is defined as the perturbation series

$$\alpha_P^p(z_2{}^0) = 1 + C_P z_2{}^0 + \mathcal{O}[(z_2{}^0)^2] \quad (4.3)$$

with the coefficient C_P generally a function of Δ_0. Freed[38] gives a detailed discussion of this type of perturbation series for the mean square end-vector distances of a polymer attached to an impenetrable surface using $G_\perp{}^0$ of (3.4a) for the limit $\Delta_0 \to 0$. It is straightforward, but tedious, to generalize these calculations to the $\Delta_0 \to \infty$ limit using (3.5a). Fourier–Laplace transform methods greatly simplify the more general calculation of C_P as a function of Δ_0, and Nemirovsky and Freed[40] thoroughly describe those techniques.

The analysis of properties P for polymers in the proximity of a plane surface is identical with that for a free chain, aside from a minor generalization involving the renormalization (see ref 40 and the Appendix) of the surface interaction. In order to confine the technical

Table I
Basic Radial Properties in Limiting Situations

polymer–surface condition (plane surface)	property P	Gaussian prefactor[a] G_P	excluded volume prefactor coefficient[b] d_P
	Tail Chain ($r_\perp^* = 0$, $r_\perp \neq 0$)		
impenetrable reflecting surface ($\Delta = 0$)	$\langle \mathbf{R}_\parallel^2 \rangle$	$(d-1)/d$	$(2\pi/3^{3/2})^{\dagger,c,d,e}$
	$\langle R_\perp^2 \rangle$	$1/d$	$-(^1/_3 + 2\pi/3^{5/2})^{c,d}$
	$\langle R_\perp \rangle$	$(2/\pi d)^{1/2}$	$4 \ln 2 - 2 - 2\pi/3^{3/2}$
	$\langle \mathbf{R}^2 \rangle = \langle R_\perp^2 \rangle + \langle R_\parallel^2 \rangle$	1	$[(d-1)a_{R_\parallel^2} + a_{R_\perp^2}]/d$
impenetrable absorbing surface ($\Delta \to \infty$)	$\langle \mathbf{R}_\parallel^2 \rangle$	$(d-1)/d$	$(2 \ln 2 - 2 + 13C)^{\dagger,d}$
	$\langle R_\perp^2 \rangle$	$2/d$	$(2 \ln 2 - 2 - 2C)^d$
	$\langle R_\perp \rangle$	$(\pi/2d)^{1/2}$	$[-(2 \ln 2 - 1) + 11C]^d$
	$\langle \mathbf{R}^2 \rangle$	$1 + 1/d$	$[(d-1)a_{R_\parallel^2} + 2a_{R_\perp^2}]/(d+1)$
penetrable noninteracting surface ($\Delta = 0$) or "free chain"	$\langle \mathbf{R}_\parallel^2 \rangle$	$(d-1)/d$	0
	$\langle R_\perp^2 \rangle$	$1/d$	0
	$\langle R_\perp \rangle$	0	0
	$\langle \mathbf{R}^2 \rangle$	1	0
	Loop Chain ($r_\perp$, $r_\perp^* = 0$)		
impenetrable reflecting surface ($\Delta = 0$)	$\langle \mathbf{R}^2 \rangle$(loop)	$(d-1)/d$	$(2 \ln 2 + 1)^{\ddagger,e}$
penetrable non-interacting surface ($\Delta = 0$)	$\langle \mathbf{R}^2 \rangle$(loop, $d_\perp = 1$)	$(d-1)/d$	$(2 \ln 2 - 1)^{\ddagger,e}$
	$\langle \mathbf{R}^2 \rangle$(loop)^{e,f}	$(d-d_\perp)/d$	$1 - \gamma - \psi(2 - d_\perp/2)$

[a] See eq 3.7 and 4.2. [b] $C \equiv 2 + 5^{1/2} \ln [(5^{1/2}-1)/(5^{1/2}+1)] \approx 0.051$. [c] Reference 38. [d] Reference 40. [e] Reference 39. [f] A hyperloop is a loop where $d_\perp$ is not restricted to equal unity. Special cases are the loop ($d_\perp = 1$), ring ($d_\perp = d$), and the free chain ($d_\perp \to 0$). ψ denotes the psi function and γ is Euler's constant.

discussion of the RG method to a minimum, we restrict attention mainly here to the $\Delta_0 \to 0$ and $\Delta_0 \to \infty$ limits where the RG scaling analysis for properties P becomes identical with that of the free chain. These limits suffice for our comparison with Monte Carlo data in section 5.

The RG theory shows that any arbitrary radial property P for a polymer having an endpoint in the proximity of an interacting plane surface has the scaling form[40,62]

$$P = G_P \langle \mathbf{R}^2 \rangle_f^{p/2} [1 + d_P u^* \lambda] + \mathcal{O}(\epsilon^2) \qquad (4.4)$$

where $\langle \mathbf{R}^2 \rangle_f$ is the mean square end-vector distance of the *perturbed* free chain with the *same* polymer–polymer interaction. In general G_P and d_P are functions of the surface interaction, and λ is a function of the binary interaction that is conveniently described in terms of a renormalized analogue of the variable z_2^0 denoted by $\bar{z}$. To first order in ϵ the crossover variable λ is[62]

$$\lambda = [4\bar{z}/(6-d)(d-2)u^*]/[1 + 4\bar{z}/(6-d)(d-2)u^*] \qquad (4.5a)$$

$$u^* = \epsilon/8 + \mathcal{O}(\epsilon^2) \qquad (4.5b)$$

where $\bar{z}$ is to be treated phenomenologically in *exactly* the same fashion as the z_2^0 in the usual TP perturbation theory. The surface interaction Δ_0 is similarly replaced by a renormalized analogue Δ without the subscript after renormalization (resummation) of the theory.

The perturbation expansion, however, is restricted to the regime $z_2^0 \ll 1$ whereas (4.4) applies for all positive $\bar{z}$. The parameter u^*, calculated from the RG theory, is seen from (4.5) to characterize the rate at which the dependence on the binary interaction saturates in the good solvent ($\bar{z} \gg u^*$) limit where the prefactor $[1 + d_P u^* \lambda]$ becomes insensitive to the binary polymer–polymer interaction. When $\bar{z} \ll u^*$, (4.5) reduces to the perturbation expansion (4.3).[62] Equations 4.4 and 4.5 are the only results from RG theory we require, and a detailed discussion of the RG analysis and the derivation of these results is presented in ref 40 and 62.

The calculations of Nemirovsky and Freed[40] and of Wang et al.[63] indicate that (4.4) applies as well to a polymer confined between parallel plates, provided the plate separation is larger than $\langle \mathbf{R}^2 \rangle_f^{1/2}$. Moreover, it is very likely that (4.4) holds for any confined region if all the confining dimensions[61] are larger than $\langle \mathbf{R}^2 \rangle_f^{1/2}$. The scaling form (4.4) is independent of the branching structure[62] in lightly branched free-chain polymers (rings, stars, etc.) to order ϵ, and this is thought to be true to all orders in ϵ-perturbation theory.[62] Thus, we expect (4.4) again to apply to these systems in the proximity of an interface. Equation 4.4, thus, has substantial generality.

B. Selected Properties for a Non-Gaussian Chain Interacting with a Surface. A tabulation of the properties $\langle R_\perp \rangle$, $\langle R_\perp^2 \rangle$, $\langle \mathbf{R}_\parallel^2 \rangle$, and $\langle \mathbf{R}^2 \rangle = \langle R_\perp^2 \rangle + \langle \mathbf{R}_\parallel^2 \rangle$ is given in Table I along with the values of the coefficients G_P [see (3.11)–(3.13)] and d_P which specify the property. The results for $\langle \mathbf{R}_\parallel^2 \rangle$ and $\langle R_\perp^2 \rangle$ for tail chains in the $\Delta \to 0$ and $\Delta \to \infty$ limits are due originally to Freed[38] and to Nemirovsky and Freed.[40] Daggers in the table denote where simple algebraic mistakes are corrected from the original references. We have also computed the quantity $\langle R_\perp \rangle$, which is important in our comparisons with Monte Carlo data and direct enumeration data in the next section. Double daggers denote the results of calculations by Eisenriegler[39] for a loop chain.

Table I also summarizes properties of a penetrable noninteracting surface, which, of course, is equivalent to a free chain. The odd moments are notably zero in contrast to the impenetrable-wall case. We also calculate $\langle \mathbf{R}^2 \rangle$ for a polymer constrained to initiate and end on a $d_\parallel$ dimension penetrable hypersurface ($\mathbf{r}_\perp^* = 0$, $\mathbf{r}_\perp = 0$) where $d_\perp$ is not restricted to be unity as in case of the impenetrable surface calculations. The "loop chain" results ($d_\perp = 1$) for the penetrable surface ($\Delta = 0$) are given by Eisenriegler,[39] but we generalize this to the case of "hyperloops" where $d_\perp$ is continuously variable. The ring and free-chain results are also special cases in the limits $d_\perp \to d$ and $d_\perp \to 0$, respectively. A suggestive correspondence with the impenetrable tail chain limit $\Delta \to \infty$ [see Table I] is found by considering the formal limit $d_\perp \to -1$ for the hyperloop to obtain G_{R^2}(hyperloop) $= (d+1)/d$ and from the definition of the ψ function, a_{R^2}(hyperloop) $= 2 \ln 2 - 2 + {}^1/_3$. We mention also that for the $\Delta \to 0$ and $\Delta \to \infty$ limits we have $\langle \mathbf{R}^2 \rangle$(tail;$z_2^0$=0;$\Delta \to \infty$) $= \langle R^2 \rangle_0$(hyperloop;$d_\perp$=1) and $\langle \mathbf{R}^2 \rangle$(tail;$\Delta$=0) $\approx \langle \mathbf{R}^2 \rangle$(hyperloop;$d_\perp$=0). An increase in Δ seems to correspond in some rough sense to a decrease in $d_\perp$ if the tail chain interacting with a surface is visualized in an effective sense as a free-chain hyperloop with continuously varying $d_\perp$. In other words, a decrease in Δ implies effectively a greater

Table II
The Exponent γ, $Q \sim (\mu/q)^n n^{\gamma-1}$

	$\gamma - 1$ (self-avoiding walk)	$\gamma - 1$ (random walk)
	Free Chain	
linear[a]	$\epsilon/8 + (13/4)(\epsilon/8)^2 + O(\epsilon^3)$	0
f-arm star[b]	$(\epsilon/16)[2 - (f-1)(f-2)] + O(\epsilon^2)$	0
hyperloops (variable $d_\perp$)		$-d_\perp/2$
(1) ring,[c] $d_\perp = d$	$-d/2 - \epsilon/4 + O(\epsilon^2)$	$-d/2$
(2) $d_\parallel = 2$, $d_\perp = d - 2$	$(2-d)/2 + O(\epsilon^2)$	$(2-d)/2$
(3) "loop chain", $d_\perp = 1$	$-1/2 + \epsilon/16 + O(\epsilon^2)$	$-1/2$
(4) $d_\perp = 2$	$-1 + O(\epsilon^2)$	-1
	Impenetrable Surface	
tail[d]		
$\Delta \to 0$	$3\epsilon/16 + (27/8)(\epsilon/8)^2 + O(\epsilon^3)$	0
$\Delta \to \infty$	$-1/2 + \epsilon/8 + (9/2)(\epsilon/8)^2 + O(\epsilon^3)$	$-1/2$
loop[d]		
$\Delta \to 0$	$-1/2 + 3\epsilon/16 + (13/8)(\epsilon/8)^2 + O(\epsilon^3)$	$-1/2$
$\Delta \to \infty$	$-3/2 + \epsilon/16 + (31/8)(\epsilon/8)^2 + O(\epsilon^3)$	$-3/2$
	Penetrable Surface	
tail[e]		
$\Delta \to 0$	$\epsilon/8 + (13/4)(\epsilon/8)^2 + O(\epsilon^3)$	0
$\Delta \to \infty$	$-1/2 + \epsilon/8 + O(\epsilon^2)$	$-1/2$
loop[e]		
$\Delta \to 0$	$-1/2 + \epsilon/16 + O(\epsilon^2)$	$-1/2$
$\Delta \to \infty$	$-3/2 + \epsilon/16 + O(\epsilon^2)$	$-3/2$

[a] References 62 and 64. [b] References 66. [c] References 65 and according to ref 85: $\gamma(\text{ring}) - 1 = -d\nu$. See also ref 8b. [d] Reference 79. [e] See text. The calculation of Kosmas[50] for $d_\parallel = 2$ and *variable* $d_\perp$ gives $\gamma(\text{tail}, z_s^0 \to \infty) = -\epsilon/4 + \mathcal{O}(\epsilon^2)$ for a penetrable surface in the self-avoiding limit.

propensity for the chain to return to the $d_\parallel = d - d_\perp$ dimensional hypersurface.

C. The Exponent γ. Another property, which can be calculated with the TP model, is the exponent γ, which characterizes the number of configurations Q of a polymer subject to the polymer–polymer and polymer–surface excluded volume constraints. The number of configurations Q relative to those for a Θ chain scales as

$$Q = \int d^d\mathbf{R}\, G(\mathbf{r}, z_2^0) \sim n^{\gamma-1}(\mu/q)^n, \qquad n \to \infty \tag{4.6}$$

where $\langle R^2\rangle_{0,f} = nl^2$, μ is the effective coordination number[18] of the self-avoiding walk, q is the coordination number for the random walk, and the subscript on the n is dropped when excluded volume is incorporated into the theory. The ratio μ/q, which dominates the magnitude of Q, is strongly dependent on small-scale details and is not considered here.

Values of γ obtained from (4.6) are given in Table II and are taken from a variety of sources. For comparison, γ for the free-chain linear,[62,64] ring,[63] and star polymer[66] are also tabulated. New results are also added for hyperloops (see section B). As mentioned before, the limits $d_\perp = d$, $d_\perp = 0$, and $d_\perp = 1$ correspond to a ring, to a free chain, and to a loop returning to a $d-1$ dimensional virtual surface, respectively. The exponent γ for a loop plays an important role in determining the order of the adsorption phase transition onto a $d_\perp$-dimension hypersurface in the lattice theory calculations of Birshtein.[67] This connection arises because γ is closely related to the probability of the walk to return to the hypersurface. For the special hyperloop dimensions corresponding to $d_\parallel = 2$ and $d_\perp = 2$ the exponent γ takes its Gaussian values to first order in ϵ.

Penetrable surface exponents γ are easily deduced without recourse to direct calculations because when $\Delta \to 0$, the surface "disappears", becoming only a virtual one so that

$$\gamma(\Delta\to 0, \text{penetrable}) = \gamma(\text{free chain}) \tag{4.7}$$

In the other extreme where $\Delta \to \infty$ there is no difference between an infinitely repulsive penetrable or impenetrable surface, and we must have

$$\gamma(\Delta\to\infty;\text{penetrable}) = \gamma(\Delta\to\infty;\text{impenetrable}) \tag{4.8}$$

First order in ϵ RG calculations for the penetrable surface ($d_\perp = 1$) with repulsive polymer–polymer and polymer–surface interactions support the prediction of these obvious limits.[63] See comments in Table II however.

Whereas the radial properties P are rather insensitive to the surface interaction for $\Delta > 0$, the exponent γ is seen from Table II to be very sensitive to the branching type and to the polymer–surface interaction. If $r_\perp{}^*$ is large ($r_\perp{}^* \gg 1$) rather than zero, then the free-chains result are found for both the penetrable and impenetrable surface. Thus, γ depends on the proximity of the chain to the surface[68] and probably also depends on surface curvature.[69]

Some caution must be taken when comparing ϵ-expansion calculations with lattice data or real polymer chain data. First of all, the ϵ-expansion method is perturbative rather than an exact treatment of the excluded volume interaction. Second order in ϵ exponents must generally be evaluated in order to provide "reasonably good predictions". On the other hand, first-order calculations of the form (4.4) are generally quite accurate in predictions for the radial properties of linear unconfined polymers because $\langle\mathbf{R}^2\rangle_f$ can be taken from order ϵ^2 calculations. Branched polymers, however, generally require a second-order calculation or the techniques of ref 62 to obtain a reliable estimate of the excluded volume prefactor coefficient d_P.

5. Comparison with Monte Carlo Simulation and Direct Enumeration Data

A. Universal Dimensionless Ratios. At present it is not possible to measure the configurational properties of isolated polymers in the vicinity of a surface.[6] Thus, our comparison with RG predictions is confined to Monte Carlo simulation and direct enumeration data. Table III presents a selection of properties considered in the previous section for limiting values of the interactions Δ and $\bar{z}$. The direct enumeration data by Lax et al.[26,27] for $\langle R_\perp{}^2\rangle^{1/2}/\langle R_\perp\rangle$, $\langle\mathbf{R}^2\rangle/\langle R_\perp{}^2\rangle$, and $\langle\mathbf{R}^2\rangle/\langle R_\perp\rangle^2$ with an absorbing boundary in the self-avoiding walk limit is seen to lie systematically in the range predicted between the $\Delta \to 0$ and $\Delta \to \infty$ limits. No attempt has been made to extrapolate these ratios to the infinite chain limit, and it is warned that many of the lattice calculations are for rather short chains ($n \leq 14$ links). Only the reproduction of qualitative trends can thus be expected. Data in the tables comes from the longest chains available in the various lattice simulation studies, and because of the uncertainty in the data, the estimates in Table III reflect precision rather than accuracy.

If we ignore the difficulty in comparison due to the shortness of the chains, the intermediate value of these ratios can be rationalized as arising from a crossover in the surface interaction. This crossover involves complicated transcendental functions in the exact calculations of Nemirovsky and Freed.[40] The approach of Kosmas[50] for the penetrable surface, on the other hand, produces a very simple analytical form in the ϵ-expansion perturbative RG theory for the crossover dependence on all of these properties. We may adopt this form as a reasonable approximate description of the surface interaction crossover for

Table III
Dimensionless Ratios

	$\langle \mathbf{R}^2\rangle^{1/2}/\langle R_\perp\rangle$	$\langle \mathbf{R}^2\rangle/\langle R_\perp^2\rangle$	$\langle \mathbf{R}^2\rangle/\langle R_\perp\rangle^2$	$\langle R_\perp{}^{max}\rangle/\langle R_\perp\rangle$	$\gamma_{R^2} = \langle \mathbf{R}^2\rangle/\langle \mathbf{R}^2\rangle_f$	$\gamma_{S^2} = \langle S^2\rangle/\langle S^2\rangle_f$	$\gamma_{S^2}/\gamma_{R^2}$
Monte Carlo Simulation and Direct Enumeration Data ($d = 3$)							
self-avoiding walk and absorbing boundary condition ($\Delta, z \to \infty$)	1.15[a]	2.39[a]	3.17[a]	1.23[a]	1.22[b]	1.03[b]	0.89[a,c]
	1.16[a]	2.37[a]	3.22[a]				
	1.18[d]	2.82[d]	3.95[d]				
self-avoiding walk and "reflecting boundary condition" ($\Delta = 0, \bar{z} \to \infty$)	1.27[a]	3.21[a]	5.20[a]	1.36[a]			0.94[a,c]
	1.25[d]	3.84[d]	6.01[d]				
Theoretical Predictions for an Impenetrable Wall ($d = 3$)[e]							
$\Delta \to \infty, \bar{z} \to \infty$	1.06	1.91	2.16		1.18		0.87
$\Delta = 0, \bar{z} \to \infty$	1.26	3.53	5.33		1.07		
$\Delta \to \infty, \bar{z} = 0$	1.13	2	2.55	1.38[f]	$^4/_3$	1.03[g]	0.773
$\Delta = 0, \bar{z} = 0$	1.25	3	4.71	1.57[f]	1		

[a] Reference 27. The estimate $\varphi_s{}^{\theta_A} \approx 0.8$ is adopted for the tetrahedral lattice (see text). [b] Reference 20. [c] The value of $\langle S^2\rangle_f/\langle \mathbf{R}^2\rangle_f = 0.135$ from ref 83. [d] Reference 21. The estimate $\varphi_s{}^{\theta_A}$ is adopted for the four-choice cubic lattice[25]. [e] See Table I. [f] Reference 71. [g] Reference 70.

the impenetrable surface. In the RG treatment of the Kosmas model for the crossover dependence on both polymer–polymer and polymer–surface interactions, we find (see Appendix) ($d = 3$, $d_\perp = 1$, $d_\parallel = 2$)

$$G_P = G_P(\Delta{=}0) + [G_P(\Delta{\to}\infty) - G_P(\Delta{=}0)]\lambda_s + \mathcal{O}(\lambda_s{}^2) \tag{5.1a}$$

and for the prefactor coefficient

$$d_P = d_P(\Delta{=}0) + [d_P(\Delta{\to}\infty) - d_P(\Delta{=}0)]\lambda_s + \mathcal{O}(\lambda_s{}^2) \tag{5.1b}$$

$$\lambda_s = (\Delta/\delta^*)/(1 + \Delta/\delta^*) \tag{5.1c}$$

where δ^* is a function of the polymer–polymer excluded volume [see Appendix and (4.5)] which determines the rate at which the effects of the surface interaction saturates. The crossover variable Δ for the Kosmas model of a penetrable surface is slightly different than Δ for the impenetrable surface model [see Appendix] when there is excluded volume, but we ignore this slight difference here. If we adopt this approximate description of the crossover, then a value of $\Delta \approx \delta^*$ with $\bar{z}$ large accounts consistently well for the intermediate values of the $\langle \mathbf{R}^2\rangle^{1/2}/\langle R_\perp\rangle$, $\langle \mathbf{R}^2\rangle/\langle R_\perp{}^2\rangle$, and $\langle \mathbf{R}^2\rangle/\langle R_\perp\rangle^2$ found in the direct enumeration data. This suggests to us that this data is in the middle of the crossover for the surface interaction.

Our RG calculations indicate that repulsive polymer–polymer interactions tend to decrease the dimensionless ratios in Table III, whereas repulsive polymer–surface interactions tend to increase them. The variation of these dimensionless properties with Δ is stronger than the variation with $\bar{z}$ since the ratios of $\langle \mathbf{R}^2\rangle$, $\langle R_\perp\rangle$, $\langle R_\perp{}^2\rangle$, etc., eliminate the strong power-law dependence of these radial properties on $\bar{z}$. It is apparent that longer chains or extrapolation techniques are required to determine if our theoretical predictions are correct for these properties. Much longer chain [$n_0 \sim \mathcal{O}(60 - 100)$units] are considered in the Monte Carlo simulation data of Eisenriegler et al.[19] Unfortunately this high-quality data is normalized in such a way that the ratios given in Table III cannot be obtained.

The Monte Carlo simulation of Clark and Lal[20] for $\gamma_{R^2} = \langle \mathbf{R}^2\rangle/\langle \mathbf{R}^2\rangle_f$ employs longer chains ($n_0 \approx 20$ links), and the agreement with theory is better in this instance. Table III also includes the ratio $\gamma_{S^2} = \langle S^2\rangle/\langle S^2\rangle_f$ for the radius of gyration, which exhibits an insensitivity to the surface interaction.[70] Assuming then that γ_{S^2} is a constant (independent of $\bar{z}$) for large Δ enables us to estimate the important ratio $\gamma_{S^2}/\gamma_{R^2}$. The direct enumeration and theoretically calculated values of $\gamma_{S^2}/\gamma_{R^2}$ agree rather well. Data is included in Table III for the ratio $\langle R_\perp{}^{max}\rangle/\langle R_\perp\rangle$ where $\langle R_\perp{}^{max}\rangle$ is the average span characterizing the average maximum distance ("thickness") of the chain from the surface. Calculations for the span of Gaussian chains are due to Rubin and Weiss.[71] The RG prediction for this property has not yet been determined, but we note the same trend is found for this span ratio as with the data for the other dimensionless ratios.

The advantage of considering the reduced ratios presented in Table III lies in the fact that although $\langle R_\perp\rangle$, $\langle R_\perp{}^2\rangle$, etc., individually depend quite strongly on the particular lattice investigated, these ratios should become independent of lattice in the long-chain limit where the coarse-grained continuum model applies. This enables us to focus on universal polymer properties.

B. Adsorption Θ Point. It is a more difficult matter to compare with available Monte Carlo data in the $\Delta \to 0$ limit. Usual Monte Carlo simulations choose[20-25] the reference state for the surface interaction to be that provided by absorbing boundary conditions where all walks that return to the surface are rejected from the ensemble averaging. A nearest-neighbor attractive surface interaction is introduced until gradually a compensation point is achieved where the polymer mimics the statistics of a reflecting barrier situated one lattice spacing from the impenetrable wall. This "adsorption Θ point" Θ_A is completely analogous to the Θ point Θ_F obtained from introducing a nearest-neighbor attractive interaction into the self-avoiding walk model. The usual Θ point occurs when the self-avoiding walks, biased by attractive interactions, mimic Gaussian chains over large length scales. Of course, in both instances there are troublesome[47,48,51] polymer–polymer and polymer–surface ternary effects for $d = 3$ which prevent the exact identification of Θ point chains and "adsorption Θ point" chains with idealized Gaussian chains and reflecting boundary conditions. The influence of these secondary effects is minimized by considering ratios of similar properties,[48] where a large measure of those ternary effects should cancel as they do for free polymers near the Θ point. The Θ point and the adsorption Θ points can then be thought of as conditions where the *effective* binary polymer–polymer and polymer–surface interactions vanish, respectively. It is only when the interactions are considered in this effective sense that meaningful comparisons can be made between the binary interaction model and simulations or real polymer experimental data.

The Θ state of polymer–polymer interactions in Monte Carlo simulation and direct enumeration calculations is defined as a critical value of φ_2 at which there is a proportionality of $\langle \mathbf{R}^2\rangle$ to n_0 or at which the second virial coefficient vanishes. These conditions have no direct analogue for the polymer surface interaction. Usually the

critical value $\varphi_s^{\Theta_A}$ is determined either from the adsorbed fraction of monomer units, which vanishes asymptotically for $T > \Theta_A$ in the limit $n_0 \to \infty$, or from closely related properties such as the average surface interaction energy per monomer unit,[17] which likewise vanishes in the $n_0 \to \infty$ limit for $T > \Theta_A$ (see ref 19 for a discussion). Below we give a heuristic analytic method of estimating $\varphi_s^{\Theta_A}$ based upon a generalization of the exact lattice chain theory with no polymer–polymer excluded volume.

There is another possibility for locating Θ_A that does not require a knowledge of the specific small-scale model parameters of the lattice. In a real polymer–solvent–surface system these small-scale parameters would be inaccessible, so it is desireable to have a means of determining the adsorption Θ point directly from large-scale observables as in the case of the polymer–polymer excluded volume interaction. At the adsorption Θ point the surface boundary condition should become effectively reflecting, so that $\varphi_s^{\Theta_A}$ can be determined by the condition that the dimensionless ratios in Table I are consistent with the theoretical predictions of a reflecting boundary. The use of this approach involves the assumptions that the influence of the ternary interaction is small in these ratios and that the chains are sufficiently long to be described by the continuous chain model. To be confident with this approach, several of these dimensionless properties should be used to see if a self-consistent definition of $\varphi_s^{\Theta_A}$ can be determined. The value of $\varphi_s^{\Theta_A}$ should also agree in the infinite-chain limit with the estimate from the adsorbed fraction of monomer units.

The latter idea is roughly illustrated in Table III, where the estimate $\varphi_s^{\Theta_A} = 0.25$ is chosen as the compensation point value of the nearest-neighbor surface interaction on a four-choice cubic lattice as determined by McCrackin[25] based upon the vanishing of the adsorption fraction as $\varphi_s \to \varphi_s^{\Theta_A}$. Reasonably good agreement is obtained with the continuum theory predictions for a reflecting impenetrable surface and the Monte Carlo simulations for this value of φ_s. [See Table III.] From a visual inspection of the direct enumeration data of Lax et al.,[26,27] we estimate $\varphi_s^{\Theta_A} \approx 0.8$ for a diamond lattice, and again rather consistent agreement is found with the predictions for a reflecting barrier. More careful simulation data for a set of universal ratios is needed to determine if this provides an adequate location of the compensation point $\varphi_s^{\Theta_A}$. Much longer chains are required than in the comparison given in Table III, which is only a schematic test of our proposed criteria.

Eisenriegler et al.[19] give another method of determining $\varphi_s^{\Theta_A}$ from large-scale observables that exploits the different scaling behavior of the radius of gyration above ($\langle S^2 \rangle \propto M^{2\nu}$, where M is the molecular weight) and below Θ_A for infinite chains. For $\varphi_s > \varphi_s^{\Theta_A}$ the infinite chain is in an adsorbed state where the embedding dimension of the polymer effectively changes as $d \to d_\parallel$, and for $T > \Theta_A$ the chain is desorbed aside from the terminal point of attachment to the surface. There is likewise a discontinuous change of ν as $\varphi_s \to \varphi_s^{\Theta_A}$ since it is a sensitive function of the confining dimension of the polymer. Eisenriegler et al.[19] find the estimate of $\varphi_s^{\Theta_A}$ obtained with this criteria to be consistent with an estimate based on the average surface interaction energy per monomer unit. For Θ-point chains this criteria cannot be used since (neglecting ternary effects) ν_Θ *is independent of* d. We now sketch a method of estimating φ_s^{Θ} directly from small-scale lattice parameters based on a heuristic generalization of the random-walk model where φ_s^{Θ} can be estimated exactly.

Polymer adsorption occurs when the enthalpic contribution of attractive polymer–surface contacts overcomes the loss of configurational entropy of the free chain. An infinite lattice polymer with no polymer–polymer excluded volume is found by Rubin[13] to have the critical dimensionless nearest-neighbor polymer–surface interaction

$$\exp(\varphi_s^{\Theta_A}) = q(\text{free})/q(\text{confined}) \tag{5.2}$$

where q is the coordination of the free chain in the absence of a boundary and q(confined) is the effective coordination number of the confined chain. Starting in $d = 3$ with a lattice of coordination number q_3 having a surface of coordination q_2, Rubin[13] shows that the effective coordination number of the confined chain is the average $q(\text{confined}) = (q_3 + q_2)/2$. Since an adsorbed segment still has remaining degrees of freedom to leave the surface, q(confined) is not to be identified with q_2. The dimensionless configurational free energy per monomer unit of a free chain is $\ln q_3$, so that (5.2) is simply a statement that a compensation point occurs when the monomer–surface enthalpic energy of interaction is equal to the entropy loss per monomer upon adsorption. The very important difference between short-range correlations in the confined and unconfined states is not included in our arguments here, but the more general case is considered by Birshtein.[67] Even without long-range excluded volume interactions the difference of short-range correlations between the confined and unconfined states can bring about large changes in the molecular dimensions.

We know of no exact method of determining $\varphi_s^{\Theta_A}$ when polymer–polymer excluded volume interactions are present. A reasonable hypothesis is provided by a generalization of (5.2) for the adsorption of a d-dimensional polymer on an impenetrable $d_\parallel$ dimension hypersurface based upon the general principle stated above. Our plausible *approximate* extrapolation involves replacing the q in (5.2) by effective values to correct for excluded volume. This approximation is

$$\exp(\varphi_s^{\Theta_A}) \approx q_d(\text{effective})/\{[q_d(\text{effective}) + q_{d_\parallel}(\text{effective})]/2\} \tag{5.3}$$

where q_d and $q_{d_\parallel}$ are the effective coordination numbers of the d-dimensional polymer and $d_\parallel$ the dimension of the surface. For self-avoiding walks, q_d(effective) is identified with μ_d, the lattice connectivity constant. Rubin[13] has generalized the discussion of adsorption onto $d_\parallel$ hypersurfaces for hypercubic lattice and finds a more complicated dependence of $\varphi_s^{\Theta_A}$ that depends, in general, on the probability for a random walk to return to the hypersurface for $d_\perp > 2$. His results imply that (5.3) is not exact, but we nonetheless expect this heuristic expression to reproduce the qualitative trend of varying the dimension of the embedding space and that of the adsorbing surface.

Equation 5.3 leads us to expect a variety of interesting adsorption phenomena that may readily be tested by MC lattice simulations. For example, the case $d \gg d_\parallel$ implies $q_d(\text{effective}) \gg q_d(\text{effective})$ or a substantial change in the number of configurational degrees of freedom of the polymer upon adsorption, and (5.3) yields $\varphi_s^{\Theta_A} \approx \ln 2$ for this case. The expected behavior of $\varphi_s^{\Theta_A}$ for high dimensions can be checked in the special limit of a random walk on a hypercubic lattice where $q_d = 2d$. Equation 5.2 then becomes

$$\exp(\varphi_s^{\Theta_A}) \approx 2/(1 + d_\parallel/d) \tag{5.4}$$

In the opposite limit where $d_\parallel \approx d$ eq 5.3 implies

$$\varphi_s^{\Theta_A} \approx 0 \tag{5.5}$$

Adsorption (or "dimensional reduction") in a high-dimensional space, when $d_\parallel \approx d$, does not involve a large

change in configurational entropy, so that the critical value of $\varphi_s^{\Theta_A}$ is expected to be quite small.

An estimate of $\varphi_s^{\Theta_A}$ for a $d = 3$ self-avoiding walk bounded by a $d = 2$ surface is found from (5.4) as

$$\exp(\varphi_s^*) \approx \mu_3/\{[\mu_3 + \mu_2]\}/2 \tag{5.6}$$

where the asterisk denotes the special limit of self-avoiding walks. On a $d = 3$ cubic lattice[72] it is found that $\mu_3 = 4.68$ and $\mu_2 = 2.64$, and (5.8) gives the estimate $\varphi_s^{\Theta_A} \approx 1.3$, which is in reasonable accord with the estimate[18] $\varphi_s^{\Theta_A} \in (1.4, 1.5)$ obtained by a direct enumeration study of the zeros of the partition function. [See Figure 2 of Middlemiss and Whittington[18].] Self-avoiding walks on a face-centered cubic lattice interacting with a square lattice surface yield[72] $\mu_3 = 10.04$, so eq 5.6 gives $\varphi_s^{\Theta_A} = 1.6$ to be compared with the numerical estimate[18] $\varphi_s^{\Theta_A} \in (1.6, 1.8)$. Ternary interactions (see section 2) undoubtedly affect the value of $\varphi_s^{\Theta_A}$ so this accuracy is probably the best we can achieve with the simple approximation (5.6). Better agreement, however, is expected for higher coordination number lattices.[55]

The shift in φ_s between the self-avoiding walk $\varphi_s^{\Theta_A}$ and Gaussian $\varphi_{s,0}^{\Theta_A}$ emerges from (5.2) and (5.6) as

$$\Delta\varphi_s \approx \varphi_s^{\Theta_A} - \varphi_{s,0}^{\Theta_A} = \ln\{(\mu_3/q_3)/[(\mu_3 + \mu_2)/(q_3 + q_2)]\} \tag{5.7}$$

which is generally a small positive number.

Finally, we mention the expected behavior of φ_s from (5.3) for a penetrable surface. Since q(confined) for a penetrable surface equals q(free), (5.2) and (5.3) become quite generally ($d_\perp = 1$)

$$\exp(\varphi_s^{\Theta_A}) \approx 1 \quad \text{or} \quad \varphi_s^{\Theta_A} \approx 0 \tag{5.8}$$

for both self-avoiding and simple random walks. This criterion for penetrable surfaces, which is exact for random walks, is discussed by Whittington[73] and is supported by Monte Carlo data[74] on a tetrahedral lattice.

C. Adsorption Threshold. For finite-length chains it is important to distinguish between the adsorption Θ point where Δ vanishes and the adsorption threshold characterizing a narrow range of the surface interactions where significant polymer adsorption occurs onto the surface. This can be understood by the analogy with the polymer–polymer interaction problem and polymer collapse. The onset of polymer collapse does not occur at the Θ point for chains of finite length, but for $d = 3$ it occurs roughly for[48] $\bar{z} \approx -3u^*/4$, where (4.5) becomes singular. From arguments similar to those of ref 48, the condition for the adsorption of a Θ chain is then

$$\Delta \approx -\delta^* \tag{5.9}$$

where (5.1c) becomes singular. Under Θ conditions $\Delta_0 = \Delta$ (see Appendix A). Taking the surface binary cluster integral to have the phenomenological dependence (see section 2) $\beta_s^0/l = (\beta_s^*/l)(T - \Theta_A)/T$, where β_s^*/l is a nonuniversal constant of proportionality, and using the definition of Δ in (3.1) imply the adsorption threshold $T_A[\Delta(T_A) \approx -\delta^*]$ occurs for

$$T_A = \Theta_A/\{1 + \delta^*/(\beta_s^*/l)(3/2)^{1/2}n_0^{\phi_s}\};$$
$$\phi_s(\bar{z} \to 0) = \tfrac{1}{2}; \qquad \delta_0^* = \pi^{1/2}/2 \tag{5.10}$$

The "crossover exponent" ϕ_s and "fixed points" δ^* are in general functions of $\bar{z}$ for chains with excluded volume and this is discussed in the Appendix. For long but finite chains (5.10) becomes

$$T_A = \Theta_A\{1 - [\delta^*/(\beta_s^*/l)(3/2)^{1/2}]n_0^{-1/2}\} \tag{5.11}$$

so that the temperatures T_A and Θ_A coincide only for infinite chains. A shift of the type is found in the Monte Carlo data of Eisenriegler et al.[19] (see Figure 18 of ref 19).

Table IV
Comparison between Block Copolymer Interblock Interactions and Polymer–Surface Interactions

first order in ϵ	γ_{R^2}(RG)	γ_{R^2} (Monte Carlo)	γ_{S^2}(RG)	γ_{S^2} (Monte Carlo)
Impenetrable Surface				
($d = 3, d_\perp = 1$)				
$\Delta = 0, \bar{z} \to \infty$	1.07[a]			
$\Delta \to \infty, \bar{z} \to \infty$	1.18[a]	1.22[a]		1.03[a]
$\Delta \to 0, \bar{z} = 0$	1[a]	1		
$\Delta \to \infty, \bar{z} = 0$	1.33[a]		1.03[a]	
Penetrable Surface				
($d = 3, d_\perp = 1$)				
$\Delta = 0, \bar{z} \to \infty$	1[b]			
$\Delta \to \infty, \bar{z} \to \infty$	1.13[b]			
$\Delta \to 0, \bar{z} = 0$	1[b]			
$\Delta \to \infty, \bar{z} = 0$	1.17[b]			
AB Diblock Copolymer (Equal-Length Blocks, $d = 3$)				
$\bar{z}_A, \bar{z}_B = 0, \bar{z}_{AB} \to \infty$	1.11[c]	1.09[d]	1.03[c]	1.02[d]
$\bar{z}_A, \bar{z}_B, \bar{z}_{AB} \to \infty$	1.06[c]	1.05[d]	1.02[c]	≤1.02[d]
$\bar{z}_{AB} = 0$	1[c]	1	1[c]	
$\bar{z}_A = 0, \bar{z}_B, \bar{z}_{AB} \to \infty$	1.08[c]		1.03[c]	

[a] See Table III. [b] Reference 78. [c] Reference 75. [d] Reference 77.

D. Impenetrable Interacting Surface and a Diblock Copolymer. The configurations of a block within a diblock copolymer have been characterized in terms of idealized "segregated" and "unsegregated" models. One specific model[70] of the segregated conformation is that the interblock interaction is similar to a polymer attached to an impenetrable surface. In this analogy an imaginary plane is visualized to be perpendicular to a line connecting the center of mass of the blocks and passing through the junction point between the blocks. Within this analogy the surface interaction parameter Δ is similar to the interblock polymer–polymer excluded volume interaction $\bar{z}_{AB}$ of the AB diblock copolymer. It is, therefore, of interest to compare the renormalization group[75] and lattice data results for the properties of a polymer attached to an impenetrable surface with the corresponding properties of a block within an AB diblock copolymer.

The properties γ_{R^2} and γ_{S^2} for block copolymers can be defined as the ratios of the dimensions of block A within an AB diblock copolymer to the dimensions of a free chain of polymer type A of the same length and having the same $\bar{z}_A$. A variety of block copolymer properties and their crossover dependence are described in ref 75, and here only limiting situations are considered. For simplicity, we specialized to the case of blocks of equal length. Table IV shows that the maximum expansion relative to the free chain for the polymer confined to the surface or within the block copolymer occurs for large Δ (or $\bar{z}_{AB}$) and small $\bar{z}$ (or $\bar{z}_A$). The absolute magnitudes of γ_{R^2} for the block copolymer and the tail polymer do not match that well, but the general trend is reproduced. A value of $\gamma_{R^2} = 1.33$ for the impenetrable surface is compared with the value $\gamma_{R^2} = 1.11$ for the block copolymer. Increasing $\bar{z}_A$ or Δ is seen to decrease γ_{R^2}, so that an increase in $\bar{z}$ (or $\bar{z}_A$) diminishes the influence of the polymer–surface or interblock interactions. This *general principle* is recognized in previous Monte Carlo studies[76,77] for block copolymers and a similar principle is evidently operative for the polymer attached to a surface. The agreement between γ_{S^2} in the two situations is striking, and we conclude that RG theory qualitatively supports the idealized segregated impenetrable surface model of the configutation of a diblock copolymer *with highly repulsive interblock interactions*. The block

Table V
The Exponent γ: Comparison with Lattice Data

free chain	γ_f(RG)	γ_f = (lattice data)
$\bar{z} \to \infty$	1.18[a]	1.16[b]
$\bar{z} \to 0$	1	1

impenetrable surface (d = 3)	γ_1(RG)	γ_1(lattice data)	$\gamma_\parallel$(RG)	$\gamma_\parallel$(lattice data)	$\gamma_1 - \gamma_f$(RG)	$\gamma_1 - \gamma_f$(lattice data)
$\bar{z} \to \infty$, $\Delta \to 0$	1.31[c]	1.44 ± 0.03[d]	−0.430			
$\bar{z} \to 0$, $\Delta \to 0$	1	≈1[d]	$^1/_2$			
$\bar{z} \to \infty$, $\Delta \to \infty$	0.695[c]	0.69 ± 0.01[d]	−0.377[c]	−0.39 ± 0.03[d]	−0.430[b,c]	−0.477[d]
$\bar{z} \to 0$, $\Delta \to \infty$	$^1/_2$	≈$^1/_2$[d]	$-^1/_2$			−0.475[e]
						−0.480[f]

[a] See Table II. [b] Reference 74. [c] Reference 79. [d] Reference 19. [e] Reference 26. [f] Reference 28.

copolymer Monte Carlo simulations by Tanaka et al. are of very high quality and the comparison between the RG theory and lattice chain data can be made with a greater degree of confidence. The agreement between the Monte Carlo data and the RG theory is most satisfactory, and we expect a similar level of agreement in the interacting surface problem once longer chains, $n_0 \gtrsim \mathcal{O}$ (50), are considered.

Table IV also presents first order in ϵ RG calculations for a penetrable surface based on the model of Kosmas,[50] where the surface interaction is treated *perturbatively* rather than exactly. A detailed discussion of these results will be given elsewhere, but here we note that the same competition between the effects of Δ and $\bar{z}$ is displayed as for the impenetrable surface and block copolymer data. The discrepancy between the value of γ_{R^2} for impenetrable and penetrable surfaces in the $\Delta \to \infty$ and $\bar{z} = 0$ limit reflects the error introduced by a first-order ϵ-expansion calculation. In this case an *exact* solution for $\bar{z} = 0$ and $\Delta \to \infty$ yields $\gamma_{R^2} = {}^4/_3$, implying a 13% error in γ_{R^2} arising from the truncation of the ϵ expansion to first order. A second order in ϵ RG calculation for the Kosmas model gives a 7% error and higher order in ϵ calculations converge uniformly to the exact limit.[78] This type of comparison is very useful for evaluating the accuracy of the ϵ-expansion procedure. More usually, when $\bar{z} \neq 0$, the ϵ-expansions and crossover structure are very similar, but the ϵ-expansions tend to be asymptotic rather than convergent. To obtain useful results for the crossover it is necessary to determine the optimal order of truncation of the ϵ-expansion.[78]

E. The Exponent γ. Table V lists lattice data from various sources for the exponents γ_{tail} and γ_{loop} for an impenetrable surface (denoted usually[40] as γ_1 and γ_{11}, respectively) in various limits. This data is compared with second order in ϵ RG predictions by Diehl and Dietrich[79] for $d = 3$ ($\epsilon = 1$) in the corresponding limits. As noted by Eisenriegler et al.,[19] the agreement of the lattice data for γ_1 and γ_{11} is good for the $\bar{z} \to 0$, $\Delta \to \infty$ limit. Early direct enumeration studies by Lax et al.[26,27] and others on rather short chains are in accord with the more recent Monte Carlo estimates of Eisenriegler et al.[19] Since Eisenriegler et al.[19] have given an extended discussion of properties related to the free energy, the discussion here is brief.

The situation for γ_1 at the compensation point $\Delta \to 0$ is less satisfying since a substantial discrepancy is found between the second-order RG result[79] and the lattice data[19] of Eisenriegler et al. It is not easy to rationalize this deviation as some kind of crossover effect since γ_1(theory) is strictly less than 1.31 for $\Delta > 0$. The proposed exact value[80] of γ_1 in $d = 2$ (neglecting ternary effects) is $\gamma_1 = {}^{61}/_{64}$, which again is less than 1.31. It is then difficult to argue that the effect is due to the chain being partially collapsed. We conjecture, however, that the very strong dependence of γ_1 on Δ (see Table V) for $\Delta \approx 0$ could somehow be related to this large discrepancy. Polymer–polymer and polymer–surface ternary effects[51] should also be investigated to gauge their contribution to $\gamma_1(\Delta=0)$.

6. Conclusion

The effect of polymer–polymer excluded volume is added to the standard diffusion equation approach[14] for describing the interaction of flexible polymers with a surface. Our general discussion indicates that this method can be applied to polymers embedded in numerous confining geometries with an interacting surface, the only restriction apparently being that the confining dimensions are larger than the mean size of the polymer. Lightly branched polymer properties can be studied with the standard Gaussian chain unperturbed model with idealized point interactions. The qualitative influence of polymer–polymer and polymer–surface ternary interaction is discussed, and methods are described that help to reduce the influence of these complicating effects. The two-parameter model is then adopted as a restricted model of certain dimensionless ratios of properties.

Our primary purpose in this paper is to compare the theoretical predictions of the two-parameter model in conjunction with the renormalization group (RG) with available Monte Carlo data before pursuing more difficult and practically important concentration-dependence calculations. Primary attention is confined to the relatively simple limiting situation of a long flexible chain attached at one end to a single flat impenetrable interacting surface in the limits of a repulsive and noninteracting surface interaction. Numerous results for these cases are tabulated based upon previous calculations, and some new results are added to make our comparison with lattice data reasonably complete.

Dimensionless ratios of radial properties (e.g., $\langle R_\perp{}^2 \rangle$, $\langle R_\perp \rangle$, and $\langle \mathbf{R}^2 \rangle$ should assume universal values in these particular limits, and theoretical predictions are checked with available direct enumeration and Monte Carlo data. Data for short chains ($n \leq 14$) indicate qualitative consistency with the predicted RG crossover behavior when the surface interaction is repulsive. Some data for longer chains ($n \leq 20$) are more consistent with the theoretical RG predictions for the long-chain limit universal ratios. Obviously, longer chains need to be considered in Monte Carlo simulations to check the theory quantitatively, and only qualitative agreement between theory and available data is found for the properties we consider. Eisenriegler et al.[19] in a complementary study have checked the renormalization group theory against a Monte Carlo simulation of much longer chains ($n \approx 60$–100) and find very good agreement for certain universal properties related to the free energy. There are, however, some notable discrepancies between the renormalization group theory and

the lattice data, which we discuss.

A description of the full crossover dependence of the lattice data is a more difficult matter than the simple idealized dimensionless ratios considered in this paper. We give a preliminary and largely heuristic discussion of the phenomenological dependence of the model variables in our theory with those in the lattice theory. Once these relations are established, a completely unambiguous comparison between the renormalization group theory and lattice data can be made over the full range of the polymer–surface and polymer–polymer interactions. Much work remains to be done, and our discussion provides only useful preliminary sketches of the problems involved and the methods that are available to help solve them.

An important part of this discussion concerns the relation between the boundary conditions conventionally used in the lattice simulations and those which are employed in the continuum diffusion equation model. As part of our comparison with Monte Carlo data for a noninteracting impenetrable surface, it is necessary to introduce criteria for determining the critical value of the nearest-neighbor interaction, where the polymer–surface interaction vanishes, in terms of large-scale observable properties involving the moments of the chain. This type of condition is analogous to the determination of the values of the polymer–polymer nearest-neighbor interaction, at which the effective polymer–polymer interaction vanishes, in terms of the scaling of the end-vector distance or the vanishing of the second virial coefficient (the conventional Flory Θ point). In order to establish the vanishing of the effective polymer–surface interaction, we require the self-consistency of the theoretical predictions with reflecting boundary conditions for as large a set of direct observables as possible. A nonrigorous method is also introduced to estimate this adsorption Θ point from the connectivity constant of the full lattice and that of the interacting surface based upon a heuristic extension of exact lattice calculations for polymers with no polymer–polymer excluded volume. The results of these analyses give encouraging self-consistent predictions which need to be studied in simulations employing longer chains to determine the quantitative limitations of these methods.

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Appendix: Excluded Volume Dependent Surface Interaction Crossover Exponent and Adsorption Threshold

The main text avoids becoming enmeshed in the technical details of the RG theory. Here we use the theory to explain the excluded volume dependence of the surface interaction crossover exponent and the adsorption threshold. Some difficulties, associated with the RG predictions for the crossover exponent, are briefly discussed.

First, following the standard RG scaling analysis (see ref 40 and 62) a renormalized surface interaction Δ is evaluated for the impenetrable surface in the form

$$\Delta \propto (d/2\pi l^2)^{1/2}\beta_s n^{\phi_s(\bar{z})} \tag{A.1}$$

where β_s and n are related to the unrenormalized (bare) variable β^0 and n_0 through renormalization factors.[40] To first order in ϵ the "crossover exponent" $\phi_s(\bar{z})$ is calculated by Nemirovsky and Freed[40] to be

$$\phi_s(\bar{z}) = {}^1/_2 - (\epsilon/16)\lambda + \mathcal{O}(\epsilon^2) \tag{A.2}$$

Diehl and Dietrich[79] evaluate ϕ_s through second order in the $\bar{z} \to \infty$ limit as

$$\phi_s(\bar{z}\to\infty) = {}^1/_2 - \epsilon/16 + [(16\pi^2 - 39)/8](\epsilon/8)^2 + \mathcal{O}(\epsilon^3) \tag{A.3}$$

When $\bar{z} \to 0$, $\phi_s(\bar{z})$ of (A.2) reduces to $\phi_s(\bar{z}=0) = {}^1/_2$ given in (2.2e).

A difficulty with the series (A.3) is the alternation in sign and the fact that the second order in ϵ contributions are *larger* than the first order ones for $d = 3$. It is, therefore, dangerous to draw any meaningful conclusion from such a series unless subjected to some kind of resummation procedure[81] or optimal order truncation. This type of ill-behaved series for the crossover exponent occurs rather generally. In the presence of both binary and large ternary interactions the crossover exponent ϕ_2 for the polymer–polymer interaction gives[82] unphysical (ϕ_2 negative) results in $d = 2$ to second order in the preturbation expansion associated with the ternary interaction. These ϵ expansions appear to be characteristically ill-behaved and the matter deserves further study (see ref 48). There is a typo in the expression for ϕ_2 given in ref 48b. The sign in front of (4 $\epsilon_3/11$) should be negative.

Monte Carlo simulation data for an impenetrable and penetrable surfaces supports a value of $\phi_s = \nu$ in $d = 3$ for self-avoiding walks[19,74]

$$\phi_s = 0.59 \pm 0.02 \text{ (impenetrable surface}^{19}\text{, } d = 3\text{, self-avoiding walk)} \tag{A.4a}$$

$$\phi_s = 0.59 \pm 0.02 \text{ (penetrable surface}^{74}\text{, } d = 3\text{, self-avoiding walk)} \tag{A.4b}$$

Kremer [see ref 84] gives the estimate $\phi_s = 0.4 \pm 0.02$ for the penetrable surface in $d = 3$, and this work should be consulted regarding the large discrepancy. However, in $d = 2$ a value of $\phi_s \approx {}^1/_2$ is found for a penetrable surface,[74] so the agreement may be fortuitous. Eisenriegler presents evidence that $\phi_s = {}^1/_2$ for Gaussian chains in $d = 3$. Although the RG theory to second order in ϵ does not predict the observed dependence of ϕ_s quantitatively, there is at least qualitative agreement with the general trend found in the lattice data.

Kosmas[50] has introduced a model of a polymer interacting with a *penetrable* surface, based upon a perturbation theory for the polymer–surface interaction, that is very similar to the TP theory of polymer–polymer excluded volume. Applying the Gell-Mann–Low RG theory to the Kosmas model of a penetrable interacting surface leads to a double crossover in Δ and $\bar{z}$ that will be described elsewhere.[78] In close analogy to the polymer collapse [see (5.1)], the condition for adsorption becomes ($d_\perp = 1$; $d_\parallel = 2$; $\epsilon_\perp = \epsilon = 1$)

$$\Delta \approx -\delta^*; \qquad \Delta = \Delta_0(1 - \lambda)^{1/4} \tag{A.5}$$

where $\delta^*(\bar{z})$ to first order in ϵ equals[78]

$$\delta^*(\bar{z}) = (\pi^{1/2}/2)\{3\lambda/4[1 - (1 - \lambda)^{3/4}]\} \tag{A.6a}$$

and

$$\delta^*(\bar{z}\to 0) = \delta_0 = (\pi^{1/2}/2) \tag{A.6b}$$

$$\delta^*(\bar{z}\to\infty) = 3\pi^{1/2}/8 \tag{A.6c}$$

The limiting fixed point values in (A.6b) and (A.6c) were determined previously by Kosmas.[50] An extra factor of $\pi^{1/2}$ occurs in (A.6b) and (A.6c) because of difference between the Δ and z_s^0 scaling variables. Interestingly this predicts that the critical value of the surface interaction at which adsorption occurs is reduced by a repulsive

polymer–polymer interaction. Note also that in the Kosmas model that ϕ_s to first order in ϵ and $\epsilon = 1$ is asymptotically

$$\phi_s(\bar{z}\rightarrow\infty) = {}^3/_8 \qquad \text{(A.6d)}$$

which is different than (A.2) derived for the impenetrable surface and for $d_\perp = 1$. More generally, the Kosmas model for variable $d_\perp$ and $d_\parallel = 2$ yields

$$\phi_s(\bar{z}\rightarrow\infty) = 3\epsilon/8 + \mathcal{O}(\epsilon^2) \qquad \text{(A.6e)}$$

A trivial generalization of the Bray–Moore–de Gennes conjecture [see ref 84] gives for $\phi_s(\bar{z} \rightarrow \infty)$

$$\phi_s(\bar{z}\rightarrow\infty) = 1 - d_\perp\nu \qquad \text{(A.7a)}$$

and for $d_\parallel = 2$

$$\phi_s(\bar{z}\rightarrow\infty) = 1 - (d-2)\nu \qquad \text{(A.7b)}$$

Equation A.7b agrees with (A.6e) to order ϵ and (A.3) is consistent with (A.7a) with $d_\perp$ fixed at unity. The ϵ-expansions for ϕ_s can therefore be quite different depending on whether or not $d_\perp$ is taken as a fixed quantity.

References and Notes

(1) Weiss, G. H.; Rubin, R. J. *Adv. Chem. Phys.* **1983**, *52*, 363.
(2) (a) Hoeve, C. A. *J. Polym. Sci.* **1977**, *61*, 389. (b) Gerber, P. R.; Moore, M. A. *Macromolecules* **1977**, *10*, 476.
(3) (a) Dolan, A. K.; Edwards, S. F. *Proc. R. Soc. London A* **1974**, *337*, 509; **1975**, *343*, 427. (b) Kitchener, J. A.; Musselwhite, P. R. "Emulsion Science"; Sherman, P., Ed.; Academic Press: New York, 1968. (c) Meier, D. J. *J. Phys. Chem.* **1967**, *71*, 1861.
(4) Casassa, E. F.; Tagami, Y. *Macromolecules* **1969**, *2*, 14.
(5) Daoud, M.; de Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1977**, *38*, 85.
(6) Takahashi, A.; Kawaguchi, M. *Adv. Polym. Sci.* **1982**, *46*, 1.
(7) Di Marzio, E. A. *J. Chem. Phys.* **1965**, *42*, 2101.
(8) de Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 1445.
(9) Eisenriegler, E. *J. Chem. Phys.* **1983**, *79*, 1052.
(10) Fisher, M. *J. Chem. Phys.* **1983**, *79*, 1052. Fisher uses a model that is very similar to the loop-train model of polymer adsorption in $d = 2$ to model a variety of interesting phenomena, such as wetting, the helix–coil transition, membrane formation, etc.
(11) (a) Roe, R. *J. Chem. Phys.* **1965**, *43*, 1591. (b) Hoeve, C.; DiMarzio, E. A.; Peyser, P. *J. Chem. Phys.* **1965**, *42*, 2558.
(12) (a) Simha, R.; Frisch, H. L.; Eirich, F. R. *J. Chem. Phys.* **1953**, *57*, 584. (b) Frisch, H. L.; Simha, R. *J. Phys. Chem.* **1954**, *58*, 507. (c) Frisch, H. L. *J. Phys. Chem.* **1955**, *59*, 663. (d) Smoluchowski, M. V. *Phys. Z.* **1916**, *17*, 557, 585. Smoluchowski first considered the problem of a random walk with reflecting and absorbing barriers in his theory of colloid coagulation. A modern discussion of this fundamental work is given by Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.
(13) (a) Rubin, R. *J. Res. Natl. Bur. Stand., Sect. B* **1965**, *69*, 301; **1966**, *70*, 237. (b) Rubin, R. J. *J. Chem. Phys.* **1965**, *43*, 2392; **1966**, *44*, 2130.
(14) de Gennes, P.-G. *Rep. Prog. Phys.* **1969**, *32*, 187. See also ref 4.
(15) Chan, D.; Mitchell, D. J.; Ninham, B. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 235.
(16) Lépine, Y.; Caillé, A. *Can. J. Phys.* **1978**, *56*, 403.
(17) (a) Whittington, S. G. *J. Chem. Phys.* **1975**, *63*, 779. (b) Hammersley, J. M.; Torrie, G. M.; Whittington, S. G. *J. Phys. A: Math Gen.* **1982**, *15*, 539. (c) Hammersley, J. M.; Whittington, S. G. *J. Phys. A: Math. Gen.* **1985**, *18*, 101.
(18) (a) Torrie, G. M.; Middlemiss, K. M.; Bly, S. H.; Wittington, S. G. *J. Chem. Phys.* **1976**, *65*, 1867. (b) Middlemiss, K. M.; Whittington, S. G. *J. Chem. Phys.* **1976**, *64*, 4684. (c) Ma, L.; Middlemiss, K. M.; Torrie, G. M.; Whittington, S. G. *J. Chem. Soc., Faraday Trans. 2* **1977**, 721. For general background see the timeless paper of: Yang, C. N.; Lee, T. D. *Phys. Rev.* **1952**, *87*, 404, 410.
(19) (a) Eisenriegler, E.; Kremer, K.; Binder, K. *J. Chem. Phys.* **1982**, *77*, 6298. (b) Binder, K., lecture notes NATO ASI Norway, 1985.
(20) Clark, A. T.; Lal, M. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1857; **1981**, *77*, 981.
(21) Mark, P.; Widwer, S. *Macromolecules* **1974**, *7*, 690.
(22) Clark, A. T.; Lal, M.; Turpin, M. A.; Richardson, K. A. *Faraday Discuss. Chem. Soc.* **1975**, *59*, 189.
(23) Clayfield, E. J.; Lumb, E. C. *J. Colloid Interface Sci.* **1966**, *22*, 285.
(24) Lal, M.; Stepto, R. F. T. *J. Polym. Sci., Polym. Symp.* **1977**, *No. 61*, 401.
(25) McCrackin, F. L. *J. Chem. Phys.* **1967**, *47*, 1980.
(26) Lax, M. *J. Chem. Phys.* **1974**, *60*, 1931, 2245, 2627, 4133.
(27) Lax, M. *Macromolecules* **1974**, *7*, 660. Lax, M. *J. Chem. Phys.* **1975**, *10*, 285.
(28) Mark, P.; Widwer, S.; Lax, M. *Macromolecules* **1975**, *8*, 946.
(29) de Gennes, P.-G. *J. Phys. Lett.* **1983**, *44*, L-241.
(30) Daoud, M.; de Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1977**, *38*, 85.
(31) Turban, L. *J. Phys. (Les Ulis, Fr.)* **1984**, *45*, 347.
(32) Pincus, P. A.; Sandroff, C. J.; Witten, T. A., Jr. *J. Phys. (Les Ulis, Fr.)* **1984**, *45*, 725.
(33) Baumgärtner, A. M. In "Applications of Monte Carlo Methods in Statistical Physics"; Binder, K., Ed.; Springer-Verlag: New York, 1984.
(34) (a) Fleer, G. J.; Scheutjens, J. *Adv. Colloid Interface Sci.* **1982**, *16*, 341. (b) Scheutjens, J.; Fleer, G. *J. Phys. Chem.* **1980**, *84*, 178.
(35) Jones, I. S.; Richmond, P. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1062.
(36) Silberberg, A. *J. Chem. Phys.* **1967**, *46*, 1105.
(37) Hoeve, C. A. *J. Polym. Sci., Part C* **1971**, *34*, 1.
(38) Freed, K. F. *J. Chem. Phys.* **1983**, *79*, 3121.
(39) Eisenriegler, E. *J. Chem. Phys.* **1985**, *82*, 1032.
(40) Nemirovsky, A. M.; Freed, K. F. *J. Chem. Phys.* **1985**, *83*, 4166.
(41) Takahashi, A.; Kawaguchi, M. *Adv. Polym. Sci.* **1982**, *46*, 1.
(42) Whittington, S. G. *Adv. Chem. Phys.* **1982**, *51*, 1. See also ref 17.
(43) Barber, M. N.; Ninham, B. "Random and Restricted Walks"; Gordon and Breach: New York, 1970.
(44) Weiss, G. H.; Rubin, R. J. *Adv. Chem. Phys.* **1983**, *52*, 363.
(45) Dickinson, E.; Lal, M. *Adv. Mol. Relax. Interact. Processes* **1980**, *17*, 1.
(46) Kosmas, K.; Freed, K. F. *J. Chem. Phys.* **1978**, *69*, 3647.
(47) (a) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *Macromolecules* **1985**, *18* 821. (b) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1985**, *83*, 5293.
(48) (a) Douglas, J. F.; Freed, K. F. *Macromolecules* **1985**, *18*, 2445. (b) Douglas, J. F.; Cherayil, B. J.; Freed, K. F. *Macromolecules* **1985**, *18*, 2455.
(49) Yamakawa, H. *J. Chem. Phys.* **1966**, *45*, 2606.
(50) Kosmas, M. K. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 563; *J. Phys. A: Math. Gen.* **1985**, *18*, 539.
(51) There are m-body surface interactions ($m > 2$) that are neglected: $\mathcal{H}_s(m>2;\text{polymer–surface}) = \sum_{m=3}^{\infty}[z_{s,m}{}^0/(m-1)!] \int_0^1 dx_1 \ldots \int_0^1 dx_{m-1}\, (2\pi)^{(m-1)(d_\perp/2)} \prod_{k=1}^{m-2}\delta[\mathbf{r}(x_k) - \mathbf{r}(x_{k+1})]\delta[\mathbf{r}_\perp(x_1)]$, where $z_{s,m}{}^0 = (d/2\pi l^2)^{(d_\perp/2)(m-1)}\beta_{s,m}{}^0 n^{\phi_{s,m}}$; $\phi_{s,m} = (m-2)(1-d/2) + (1-d_\perp/2)$ and $\beta^\circ_{s,m}$ is a m-body surface cluster. For $d = 3$ and $d_\parallel = 2$ the surface ternary interaction is marginal, and the interactions for $m > 3$ are irrelevant as in the free-chain theory [see ref 48].
(52) McQuarie, D. "Statistical Mechanics"; Harper and Row: New York, 1973. For a discussion of the Ursell–Mayer cluster theory in continuously variable dimension see: Stillinger, F. H. *J. Math. Phys.* **1977**, *18*, 1225.
(53) Freed, K. F. *J. Phys. A: Math. Gen.* **1985**, *18*, 871.
(54) Jenssens, M.; Bellemans, A. *Macromolecules* **1976**, *9*, 303.
(55) Douglas, J. F.; Freed, K. F., manuscript in preparation.
(56) (a) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1971. (b) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *26*, 1067. The mean field theory in the theory of nonideal gases corresponds to the limit $\Lambda_2 \rightarrow \infty$. [See: Stanley, H. E. "Introduction to Phase Transitions and Critical Phenomena"; Oxford University Press, New York, 1971. Kac, M.; Uhlenbeck, G. E.; Hemmer, P. C. *J. Math. Phys.* **1963**, *4*, 216.] In the lattice model the equivalent of the limit is obtained by taking the coordination number to be large, corresponding to high dimensionality. In these limits the values of φ_2 are infinitesimal in the range $\varphi_2 \in (0,\varphi_2^\Theta)$ [see (2.3a)], so that (2.3b) is obtained exactly in the mean field approximation as obtained previously by Flory.
(57) Kurata, M.; Stockmayer, W. H. *Adv. Polym. Sci.* **1963**, *3*, 196.
(58) Guttman, C. M. *J. Stat. Phys.* **1984**, *36*, 717.
(59) Berry, G. C. *J. Chem. Phys.* **1967**, *46*, 1338.
(60) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180. See also: Perzynski, R.; Adam, M.; Delsanti, M. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, 129.
(61) For example, consider a two-parallel plate geometry, with L the distance between plates. The expansion of (4.1) is about a d-dimensional reference state and is appropriate as long as the length of the chain $\langle \mathbf{R}^2\rangle_f^{1/2}$ is smaller than the confining size $\langle \mathbf{R}^2\rangle_f^{1/2} \leq L$. In the opposite limit of $\langle \mathbf{R}^2\rangle_f^{1/2} \gg L$ with

$L \gg a$ (a is a monomer size), the system displays $(d-1)$-dimensional properties (a "dimensional reduction"), and expansions about a d-dimensional reference state are inappropriate. These difficulties manifest themselves in renormalization group calculations having first-order (in the excluded volume) corrections to many quantities which become much larger than zeroth-order contributions in the $\langle \mathbf{R}^2 \rangle_f^{1/2} \gg L$ regime. The mathematical origin of this effect is that, as $\langle \mathbf{R}^2 \rangle^{1/2} \sim \mathcal{O}(L)$, the normal end-vector distribution scales as $G_\perp(R/L)$ rather than $G_\perp(R/\langle \mathbf{R}^2 \rangle^{1/2})$. See Dolan and Edwards[3] for a relevant discussion. An effective free energy functional method has been recently introduced by two of us [Nemirovsky, A. M.; Freed, K. F. *J. Phys. A: Math. Gen.*, in press; *Nucl. Phys. B*, in press] to remedy related problems in critical phenomena. We plan to utilize similar methods to study the "dimensionally reduced" regime of polymers strongly adsorbed onto surfaces and confined in some bounded geometries where $L \lesssim \mathcal{O}(\langle \mathbf{R}^2 \rangle_f^{1/2})$.

(62) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 1854, 2344; **1985**, *18*, 201.
(63) Wang, Z.; Nemirovsky, A. M.; Freed, K. F., unpublished work. The magnetic analogue, of the penetrable interacting surface, a magnetic system with a plane of defects, is treated by: Diehl, H. W.; Dietrich, S.; Eisenriegler, E. *Phys. Rev. B: Condens. Matter* **1983**, *27*, 2937.
(64) (a) de Gennes, P.-G. *Phys. Lett. A* **1972**, *36*, 339. (b) Wilson, K. G. *Phys. Rev. Lett.* **1972**, *28*, 548.
(65) Lipkin, M.; Oono, Y.; Freed, K. F. *Macromolecules* **1981**, *14*, 1270.
(66) Miyake, A.; Freed, K. F. *Macromolecules* **1983**, *16*, 1228. See also: Lipson, J. E. G.; Whittington, S. G.; Wilkinson, M. K.; Martin, J. L.; Gaunt, D. S. *J. Phys. A* **1985**, *18*, L469.
(67) Birshtein, T. M. *Macromolecules* **1979**, *12*, 715; **1983**, *16*, 45. According to the calculations of Birshtein, the phase transition order for adsorption of *Gaussian* chains onto a $d_\parallel$ dimension hypersurface is (implicity) given for $d = 3$ by $1/|\gamma_{\text{hyperloop}}|$. See: Fisher, M. E. *J. Chem. Phys.* **1969**, *45*, 1469 and Poland, D.; Scheraga, H. *J. Chem. Phys.* **1966**, *45*, 1456 for a discussion of the order of the helix-coil transition. See also: Gorbunov, A. A.; Zhulina, E. B.; Skvortsov, A. M. *Polymer* **1982**, *23*, 1173 for a discussion of the effect of surface curvature on $\varphi_s^{\theta_a}$.
(68) A direct calculation, which generalizes a result of Freed, for $r_\perp^* = 0$, gives for a chain in the proximity of a noninteracting surface ($\Delta \to 0$), $Q = Q_{\text{tail}}[1 - (r_\perp^*)^2 u^* \lambda/16 + \mathcal{O}(\epsilon^2)] \sim n^{\gamma_1 - 1}(\mu/q)^n$; $r_\perp^* \ll 1$. At larger distances from the surface we have $Q = Q_{\text{free}} \sim n^{\gamma - 1}(\mu/q)^n$; $r_\perp^* \gg 1$. The exponent γ as a function of $r_\perp^*$ can be constructed from these limiting forms in a similar fashion as the calculation of γ as function of Δ for tail chains. The latter can be deduced from the work of: Goldschmidt, Y. Y. *Phys. Rev. B: Condens. Matter* **1983**, *28*, 4052. It is expected that the dependence of γ on surface curvature gives rise to a similar awkward description of crossover.
(69) Symanzik, K. *Nucl. Phys. B* **1981**, *B190*.
(70) Tanaka, T. *Macromolecules* **1977**, *10*, 51.
(71) Rubin, R.; Weiss, G. W. *J. Chem. Phys.* **1983**, *78*, 2039.
(72) McKenzie, D. S. *Phys. Rep.* **1976**, *27*, 37.
(73) Hammersley, J. M.; Torrie, G. M.; Whittington, S. G. *J. Phys. A: Math. Gen.* **1982**, *15*, 539. This reference shows that (5.4) holds exactly when $d_\perp = 1$.
(74) (a) Ishinabe, T.; Whittington, S. G. *J. Phys. A: Math. Gen.* **1981**, *14*, 439. (b) Ishinabe, T. *J. Chem. Phys.* **1984**, *80*, 1318. See also ref 84.
(75) Douglas, J. F.; Freed, K. F., submitted. For some related properties see: Joanny, J.; Liebler, L.; Ball, R. *J. Chem. Phys.* **1984**, *81*, 4640.
(76) (a) Bendler, J.; Šolc, K.; Gobush, W. *Macromolecules* **1977**, *10*, 635. (b) Bendler, J.; Šolc, K.; Gobush, W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1977**, *18*, 319. See also ref 77.
(77) (a) Tanaka, T.; Kotaka, T.; Inagaki, H. *Macromolecules* **1976**, *9*, 561. (b) Tanaka, T.; Kotaka, T.; Ban, K.; Hattori, M.; Inagaki, H. *Macromolecules* **1977**, *10*, 950. (c) Tanaka, T.; Kotaka, T. *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, *20*, 9. (d) Tanaka, T.; Omoto, M.; Inagaki, H. *Macromolecules* **1979**, *12*, 147. (e) Fukuda, T.; Inagaki, H. *Pure Appl. Chem.* **1983**, *55*, 1541.
(78) Douglas, J. F.; Wang, S. Q.; Freed, K. F., "Test of Renormalization Group Crossover Dependence: Comparison with Exact Solution for a Polymer Attached to a Penetrable Interacting Hypersurface", *Macromolecules*, to appear.
(79) Diehl, H. W.; Dietrich, S. *Z. Phys. B: Condens. Matter* **1981**, *42*, 65; **1983**, *50*, 117. Diehl, H. W.; Dietrich, S. *Phys. Rev. B: Condens Matter* **1981**, *24*, 2878. See also: Reeve, J. S.; Guttmann, A. J. *Phys. Rev. Lett.* **1980**, *45*, 1581; *J. Phys. A: Math Gen.* **1981**, *14*, 3357.
(80) Cardy, J., preprint. See ref 19. The referees note that there are still some questions to be resolved in the Cardy derivation of γ_1, so this result should be considered tentative.
(81) LeGuillou, J. C.; Zinn-Justin, J. *Phys. Rev. B: Condens. Matter* **1980**, *21*, 3976; *J. Phys. Lett.* **1985**, *46*, L-137.
(82) Lewis, A. L.; Adams, F. W. *Phys. Rev. B: Condens. Matter* **1978**, *18*, 5099.
(83) (a) Wall, F. T.; Erpenbeck, J. J. *J. Chem. Phys.* **1958**, *30*, 634, 637. (b) Domb, C.; Aioe, F. T. *J. Chem. Phys.* **1971**, *54*, 5051.
(84) (a) Kremer, K. *J. Chem. Phys.* **1985**, *83*, 5882. (b) Burkhardt, T. W.; Eisenriegler, E. *Phys. Rev. B* **1981**, *24*, 1236.
(85) de Gennes, P. G. "Scaling Concepts in Polymer Physics" Cornell University Press: Ithaca, NY, 1979.
(86) Kuhn, W. *Kolloid Z.* **1934**, *68*, 2.

Conformational Entropy of Ring Polymers

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ABSTRACT: An expression for the partition function of ring polymers is derived for the treatment in which bond lengths and bond angles are kept fixed and only dihedral angles are variables. When there are n rotatable backbone dihedral angles in a ring polymer, only $(n-6)$ of them are independent and the values of the remaining six angles can be determined as functions of $(n-6)$ angles chosen as independent variables. The conformational energy E is then a function of these $(n-6)$ independent variables. However, the partition function is not given as an integral of $\exp(-\beta E)$ over the space of the $(n-6)$ variables. In fact this integral depends on the choice of $(n-6)$ independent variables, while the correct partition function should be independent of the choice. The derived expression is independent of the choice of independent variables.

The theoretical method of conformational energy analysis has been applied successfully to many problems of biopolymers, including proteins and peptides.[1] The method has been developed to calculate not only conformational energy but also conformational entropy by formulating the method of calculating the partition function.[2] When bond lengths and bond angles are kept fixed and only dihedral angles are treated as variables in such analyses, ring polymers require special considerations, because not all of the backbone dihedral angles are independent. When there are n rotatable backbone dihedral angles in a ring polymer, only $(n-6)$ of them are independent and the values of the remaining six angles can be determined as functions of the $(n-6)$ angles chosen as independent variables. The problem of expressing dependent dihedral angles as explicit functions of independent dihedral angles was solved previously.[3] Therefore, conformational energy E is then given as a function of the

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