there the slow modes overwhelm the fast ones completely.

(13) $\tilde{w}_2$ determined from the $A_2$ data was used to evaluate $G_{2,\mathrm{sol}}^*$ because $A_2$ is less sensitive to the fast relaxation modes than $\eta_2$.[12]

(14) Both slow and fast modes contribute to the *empirically determined* $G_{2,\mathrm{m}}^*(\omega)$, although the contribution of the fast modes is not significant at low $\omega$. Thus, some fast modes, which should contribute to $\Delta G_{2,\mathrm{bB}}^*$, were lost from $\Delta G_{2,\mathrm{bB}}^*$ as $G_{2,\mathrm{sol}}^*$ represented by $G_{2,\mathrm{m}}^*$ (eq 20) was subtracted from $G_{2,\mathrm{bB}}^*$. (Analyzing the spectra $H_{\mathrm{bB}}$ itself, we can avoid this difficulty.[3,4]) However, in practical purposes, this problem is not serious in the present analysis on bB with small $w_2$ (curves d in Figures 10 and 12) because $G_{2,\mathrm{sol}}^*$ is already much smaller than $G_{2,\mathrm{bB}}^*$ at high $\omega$: The $\Delta G_{2,\mathrm{bB}}^*$ curve would not change much even if we use the $G_{2,\mathrm{sol}}^*$ to which only the slow modes contribute.

(15) For bB with much larger $M_{\mathrm{w2}}/M_{\mathrm{w1}}$ ratio we observed the wedge-shaped $G_{2(i)}^*$ curve more clearly.[11]

(16) Struglinski, M. J.; Graessley, W. W. *Macromolecules* **1985**, *18*, 2630.

(17) Montfort, J.-P.; Marin, G.; Monge, P. *Macromolecules* **1984**, *17*, 1551.

(18) The characteristic time of the $G_{2(i)}^*$ curve increases with increasing $M_{\mathrm{w2}}$.[11] This result also suggests that the Rouse-like motion of the 2-chain due to partial tube renewal is not confined between the adjacent 2–2 entanglement points.

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# Flexible Polymers with Excluded Volume at a Penetrable Interacting Surface

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ABSTRACT: Polymers, terminally attached to a $d_\parallel$-dimension penetrable interacting hypersurface, are described by using the two-parameter model of excluded volume, a pseudopotential polymer–surface interaction model, and the renormalization group method. The dimensionality of the hypersurface is fixed as $d_\parallel = 2$, so that the $\epsilon$-expansion ($\epsilon = 4 - d$ with $d$ the dimension of space) method can be applied to both the polymer–polymer and polymer–surface interactions. Then the mean-square end-to-end vector distance $\langle \mathbf{R}^2 \rangle$ is calculated to first order in $\epsilon$ as a function of polymer–surface and polymer–polymer interactions. The result is compared to $\langle \mathbf{R}^2 \rangle$ for a terminally attached polymer at an impenetrable interacting surface. An increase in the chain expansion due to *repulsive* excluded volume interactions leads to a *decrease* in the effects of repulsive polymer–surface interactions on the polymer dimensions. This phenomenon is an apparent consequence of the lower density of the chain upon expansion and the resultant lower probability of the chain encountering the surface. Scaling arguments, on the other hand, indicate that *attractive* surface interactions *amplify* the effect of the excluded volume interaction.

## I. Introduction

The theoretical description of isolated polymers in the presence of an interacting boundary has been considered by using both lattice random walk and continuum random walk models. Rubin[1] has studied lattice random walks interacting with an impenetrable surface for the full range of the polymer–surface interaction and has calculated many of the important configurational properties of ideal polymers with no polymer–polymer interactions. de Gennes[2] and Lépine and Caillé[3] have also made important contributions to the continuum formulation of the random walk model of a chain interacting with an impenetrable surface.

Some recent work has focused on extending these earlier calculations to consider penetrable surfaces. Hammersley et al.[4] give exact lattice random walk model calculations for an interacting penetrable surface. Kosmas[5] introduces a continuum model of a Gaussian polymer interacting with a penetrable surface of continuously variable dimension $d_\parallel$, and Nemirovsky and Freed[6] consider the exact analytic treatment of the special case of penetrable and impenetrable surfaces having a dimension one less than that of the embedding space, $d_\parallel = d - 1$. More recently, Douglas et al.[7] studied the exact treatment of the penetrable interacting surface model[5] for Gaussian chains where the adsorbing surface dimension $d_\parallel$ is a variable. Wang et al.[8] generalize the Nemirovsky and Freed[6] calculation by including three surface interactions, one for each side of the surface and one describing the "penetrability" of the surface. The penetrable surface model[5,7] with variable $d_\parallel$ can be similarly extended to include three surface interaction parameters, but this is left for future work.

The introduction of polymer–polymer excluded volume interactions is an important extension of the lattice random walk and continuous Gaussian chain models. Hammersley et al.[4] perform exact calculation for lattice self-avoiding walks (SAW's) for both penetrable and impenetrable surfaces, and there are numerous Monte Carlo and direct enumeration calculations[9] for SAW's interacting with an impenetrable surface. Recent lattice calculations by Ishinabe[10] and Kremer[11] consider SAW's interacting with a penetrable surface.

The development of renormalization group (RG) methods enables the extension of surface-interacting Gaussian chain models to incorporate the excluded volume interaction, provided the polymer–polymer interactions are not strongly attractive.[7,12] The first extensive treatment of surface-interacting polymers by Eisenriegler et al.[13] uses the polymer–magnet analogy in conjunction with Monte Carlo and scaling methods to consider numerous properties of surface-interacting polymers. Freed[14] employs the equivalent two-parameter (TP) model of excluded volume and evaluates some basic radial properties such as $\langle \mathbf{R}^2 \rangle$ and the end-to-end vector distribution function for a polymer at an impenetrable reflecting surface where the polymer–surface interaction vanishes. Eisenriegler[15] calculates some similar properties in this limit within the magnetic analogy model and also considers the concentration dependence of polymers near impenetrable surfaces. Nemirovsky and Freed[6] generalize the TP approach to treat the full "double crossover dependence" of polymer properties on the polymer–polymer and polymer–surface

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interactions where the impenetrable surface interaction is treated *exactly* and where the excluded volume interaction is treated by using the RG theory and $\epsilon$-expansion procedure. Many of the results from these studies of impenetrable-surface-interacting polymers are reviewed in ref 9.

Here we generalize the previous work of Nemirovsky and Freed[6] and of Douglas et al.[7] to the case of polymers with excluded volume interacting with a *penetrable* interacting surface where the surface dimension $d_{\parallel}$ is fixed at $d_{\parallel} = 2$, so that the excluded volume and polymer–surface interactions can both be treated by using the $\epsilon$-expansion perturbation theory. Calculations using this approach lead to far simpler expressions for the multiple interaction crossover than those found by Nemirovsky and Freed[6] for the impenetrable surface.

The surface interaction and excluded volume models are introduced in section II. Next, the moments of the end-to-end vector distance for repulsive polymer–surface and excluded volume interactions are calculated in section III and compared with the results of Nemirovsky and Freed[6] for $\langle \mathbf{R}^2 \rangle$ in the case of an impenetrable plane surface in $d = 3$. A qualitative description of the attractive interaction regime is given in section IV.

## II. The Model

The reference model is a continuous Gaussian chain backbone that is perturbed by a $\delta$-function pseudopotential for the polymer–surface interaction. Phenomenological 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 subsumed into the model variables to obtain a universal description of large-scale properties.

The continuous chain configuration is specified by the position vector $\mathbf{R}(x)$ of the chain segment at a contour distance $x$ along a chain of 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 $\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}$ of a free unperturbed chain as

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

The dimensionless configurational Hamiltonian for the polymer–surface interactions in these units equals

$$H/k_{\mathrm{B}}T = H_0 + H_{\mathrm{s}}(\text{polymer–surface}) + H_2(\text{polymer–polymer}) \qquad (2.2a)$$

where the unperturbed portion

$$H_0 = (1/2)\int_0^1 \mathrm{d}x \, |\mathrm{d}\mathbf{r}(x)/\mathrm{d}x|^2 \qquad (2.2b)$$

reflects chain connectivity and where $k_{\mathrm{B}}T$ is the absolute temperature in energy units.

The interacting surface is a hypersurface of dimension $d_{\parallel}$ 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 $\mathbf{r}_{\perp}(x)$ is the projection onto an orthogonal space of dimension $d_{\perp}$. Within a continuum model representation similar to that introduced by Edwards[16] for the polymer–polymer excluded volume interaction, the surface interaction portion of the Hamiltonian equals[5-7]

$$H_{\mathrm{s}}(\text{polymer–surface}) = z_{\mathrm{s}}^0 \int_0^1 \mathrm{d}x \, \delta(\mathbf{r}_{\perp}(x)](2\pi)^{d_{\perp}/2} \qquad (2.2c)$$

where the dimensionless polymer–surface interaction parameter $z_{\mathrm{s}}^0$ is defined as

$$z_{\mathrm{s}}^0 = (d/2\pi l^2)^{d_{\perp}/2} \beta_{\mathrm{s}}^0 n_0^{\epsilon_{\perp}/2}$$
$$\epsilon_{\perp} = 2 - d_{\perp} = (2 + d_{\parallel}) - d \qquad (2.2d)$$

Here $\beta_{\mathrm{s}}^0$ is the polymer–surface binary cluster integral, and $\delta[(\mathbf{r}_{\perp}(x)]$ is a $d_{\perp}$-dimensional $\delta$-function. Short-range correlations, such as the constraint against immediate reversal in lattice chains and restrictions on bond angles, in real polymers are as usual implicitly absorbed into the definition of the effective step length $l$. The number of statistical segments $n_0$ is related to the chain contour length $N_0$ and to the free Gaussian chain mean-square end-vector distance $\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}$ through the definitions

$$\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}} \equiv N_0 l \equiv n_0 l^2 \qquad (2.2e)$$

The polymer–polymer interaction is modeled by

$$H_2(\text{polymer–polymer}) = (z_2^0/2)\int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}x' \, (2\pi)^{d/2} \delta[\mathbf{r}(x) - \mathbf{r}(x')] \qquad (2.3a)$$

where $z_2^0$ of the two-parameter (TP) theory has the traditional polymer theory definition ($\epsilon = 4 - d$)

$$z_2^0 = (d/2\pi l^2)^{d/2} \beta_2^0 n_0^{\epsilon/2} \qquad (2.3b)$$

with $\beta_2^0$ the polymer–polymer binary cluster integral. For $d_{\parallel} = 2$ we have $\epsilon_{\perp} = \epsilon$ [see (2.2d)], which is the special case necessarily considered for RG expansions in both excluded volume and surface interactions.[5,7]

## III. Repulsive Polymer–Polymer and Polymer–Surface Interactions

The end-vector distribution function $G(\mathbf{r},z_2^0,z_{\mathrm{s}}^0)$ for a terminally attached Gaussian chain with excluded volume interacting with a penetrable surface is defined in terms of the model Hamiltonian $H$ of (2.2) by

$$G(\mathbf{r},z_2^0,z_{\mathrm{s}}^0) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(1)=\mathbf{r}} \mathcal{D}[\mathbf{r}] \exp[-H(z_2^0,z_{\mathrm{s}}^0)/k_{\mathrm{B}}T] \qquad (3.1)$$

where $\mathcal{D}[\mathbf{r}(x)]$ is the Wiener conformational measure. We obtain the surface and excluded volume interaction perturbation series by expanding the interaction terms in a formal Taylor expansion in $z_2^0$ and $z_{\mathrm{s}}^0$ as

$$G(\mathbf{r},z_2^0,z_2^0) = \int_{\mathbf{r}(0)=0}^{\mathbf{r}(1)=\mathbf{r}} \mathcal{D}[\mathbf{r}(x)] \exp(-H_0) \times (1 - H_{\mathrm{s}} - H_2 + H_2H_{\mathrm{s}} + H_2^2/2! + H_{\mathrm{s}}^2/2! + \ldots) \qquad (3.2)$$

Before the double expansion in $H_{\mathrm{s}}$ and $H_2$ is evaluated, it is useful to review some results for the previously studied limits of either $z_2^0 = 0$ or $z_{\mathrm{s}}^0 = 0$ as the more complicated general theory must recover these limiting behaviors.

**A. Vanishing Excluded Volume Interaction.** The end-to-end vector distance $\langle \mathbf{R}^2 \rangle$ is an important polymer property for characterizing the average dimensions of the polymer, even though it is only an observable for lattice polymers. It is convenient to calculate the $\langle \mathbf{R}_{\parallel}^2 \rangle$ and $\langle \mathbf{R}_{\perp}^2 \rangle$ components of $\langle \mathbf{R}^2 \rangle$ separately where these are the projections of $\langle \mathbf{R}^2 \rangle$ onto the $d_{\parallel}$- and $d_{\perp}$-dimension subspaces.

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}_{\parallel}^2 \rangle + \langle \mathbf{R}_{\perp}^2 \rangle \qquad (3.3a)$$

The end-vector distance is easily calculated by factoring the unperturbed Gaussian end-to-end vector distribution for a free chain as[5-7]

$$G[\mathbf{r}, x, z_2^0 = 0, z_{\mathrm{s}}^0 = 0] = G_{\perp}^0[\mathbf{r}_{\perp}, x] G_{\parallel}^0[\mathbf{r}_{\parallel}, x] \qquad (3.3b)$$

or explicitly we have

$$G[\mathbf{r}, x, z_2^0 = 0; z_s^0 = 0] = [(2\pi x)^{-d_\perp/2} \exp(-\mathbf{r}_\perp{}^2/2x)][(2\pi x)^{-d_\parallel/2} \exp(-\mathbf{r}_\parallel{}^2/2x)] \tag{3.3c}$$

In a previous paper we calculate $\langle \mathbf{R}_\perp{}^2 \rangle$ and several other properties for $z_2^0 = 0$ through infinite order in $z_s^0$. For illustration we recall $\langle \mathbf{R}_\perp{}^2 \rangle$, which is equal to[7]

$$\langle \mathbf{R}_\perp{}^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}\{\sum_{n=0}^{\infty} (-1)^n [z_s^0 \Gamma(\epsilon_\perp/2)]^n / \Gamma(2 + n\epsilon_\perp/2)\}/Q \tag{3.4a}$$

where the partition function $Q(z_s^0)$ is found as[7]

$$Q(z_s^0) = \sum_{k=0}^{\infty} (-1)^k [z_s^0 \Gamma(\epsilon_\perp/2)]^k / \Gamma(1 + k\epsilon_\perp/2) \tag{3.4b}$$

These series have an infinite radius of convergence for $\epsilon_\perp > 0$ and are expressible[7] in terms of the Mittag–Leffler function whose properties are summarized by Hardy.[17] A second order in the $\epsilon_\perp$-expression is obtained by applying the RG theory to (3.4) to third order in $z_s^0$. From previous work[7] this expansion for $\langle \mathbf{R}_\perp{}^2 \rangle$ yields

$$\langle \mathbf{R}_\perp{}^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}[1 + u_s^* \lambda_s + (u_s^*)^2 (2\lambda_s{}^2 - \lambda_s) + \mathcal{O}(\epsilon_\perp{}^3)] \tag{3.5a}$$

$$\lambda_s = \zeta_s/(1 + \zeta_s) \qquad u_s^* = \epsilon_\perp/2 \tag{3.5b}$$

where the "renormalized" variable $\zeta_s$ can be written (see Appendix and ref 7) directly in terms of phenomenological bare variables ($\zeta_s \equiv z_s^0/u_s^*$) to facilitate comparison with the exact solution (3.4a). Our first-order calculations below for the double crossover on polymer–polymer and polymer–surface interactions must recover (3.5) to first order in $\epsilon$ in the limit of vanishing excluded volume.

The RG approximation (3.5a) reproduces the exact result (3.4) reasonably well for $z_s^0 \geq 0$. The largest error occurs in the large $z_s^0$ limit where (3.4) reduced to[7]

$$\langle \mathbf{R}_\perp{}^2 \rangle = (d_\perp \langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}/d)/(1 - \epsilon_\perp/2) \tag{3.5c}$$

Expanding (3.5c) to order $\epsilon_\perp{}^2$ yields

$$\langle \mathbf{R}_\perp{}^2 \rangle = (d_\perp \langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}/d)[1 + \epsilon_\perp/2 + (\epsilon_\perp/2)^2 + \mathcal{O}(\epsilon_\perp{}^3)] \tag{3.5d}$$

which is also the $z_s^0 \to \infty$ limit of (3.5a). For $\epsilon_\perp = 1$, eq 3.5d differs from the exact expression in (3.5c) by 7% (see subsection D), and a comparison for the full crossover in $z_s^0$ is presented in ref 7. The parallel component $\langle \mathbf{R}_\parallel{}^2 \rangle$ is the same as for a free chain and is readily found as

$$\langle \mathbf{R}_\parallel{}^2 \rangle = (d_\parallel/d)\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}} \tag{3.5e}$$

We then obtain the RG prediction for the end-to-end vector distance $\langle \mathbf{R}^2 \rangle$ as the sum of (3.5a) and (3.5e).

**B. Vanishing Surface Interaction.** The limit of vanishing surface interactions for a penetrable surface corresponds to a polymer in free space. This free chain limit has been studied in previous work,[18-20] and its description exhibits a very similar analytic structure to the surface interaction theory of the previous subsection. For example, the dimensionless ratio of $\langle \mathbf{R}^2 \rangle_\mathrm{f}$ and the radius of gyration $\langle S^2 \rangle_\mathrm{f}^{1/2}$ of a free chain is calculated to order $\epsilon$ to have the form[19-22]

$$\langle \mathbf{R}^2 \rangle_\mathrm{f}/6\langle S^2 \rangle_\mathrm{f} = 1 + (u_2^*/12)\lambda_2 + \mathcal{O}(\epsilon^2) \tag{3.6}$$

$$u_2^* = \epsilon/8 + \mathcal{O}(\epsilon^2) \qquad \lambda_2 = \zeta/(1 + \zeta) \tag{3.7}$$

The excluded volume variable $\zeta$ of the RG theory is the same as introduced by Oono and Freed[22] and is defined explicitly in the Appendix. Douglas and Freed[19] show that

$$\zeta = z_2^0/u_2^* \tag{3.8}$$

which gives the connection between the phenomenological bare and RG excluded volume variables. Using this relation we see, for example, that (3.6) is equivalent to an expression given first by de Cloizeaux.[20]

**C. Combined Influence of Polymer–Polymer and Polymer–Surface Interactions.** The inclusion of the polymer–polymer excluded volume interaction (2.3a) into the Hamiltonian (2.2a) makes the problem of a surface-interacting polymer no longer exactly solvable. Moreover, there is at present no analytic RG method enabling the treatment of two interactions having different critical dimensionalities, i.e., of $\epsilon \neq \epsilon_\perp$. Kosmas[5] recognized that if $d_\parallel$ is fixed at $d_\parallel = 2$, so that $\epsilon_\perp = \epsilon$, then it is possible to proceed with standard RG methods for this important special case.

The perturbative calculation for $\langle \mathbf{R}_\perp{}^2 \rangle$ is based upon (3.2) for $d_\parallel = 2$ and leads to

$$\langle \mathbf{R}_\perp{}^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}[1 + z_s^0 + (2/\epsilon - 1)z_2^0 + (2/\epsilon) \times (z_s^0)^2 + (-6/\epsilon^2 + 11/2\epsilon)(z_2^0)^2 + \ldots] \tag{3.9a}$$

where we neglect second-order terms in the $\{z_i\}$ interactions such as the cross term $z_2^0 z_s^0$ which are nonsingular in $\epsilon$ because these terms do not contribute in our RG calculations to first order in $\epsilon$. Equation 3.9a reduces in the $z_s^0 \to 0$ limit to a perturbation expansion for the $\langle \mathbf{R}_\perp{}^2 \rangle$ component of a free perturbed chain $\langle \mathbf{R}^2 \rangle_\mathrm{f}$, which is given by des Cloizeaux as[20]

$$\langle \mathbf{R}^2 \rangle_\mathrm{f} = \langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}[1 + (2/\epsilon - 1)z_2^0 + (-6/\epsilon^2 + 11/2\epsilon)(z_2^0)^2 + \ldots] \tag{3.9b}$$

while for $z_2^0 \to 0$ eq 3.9a reduces to the $\epsilon$-expanded form of (3.4a) to order $(z_s^0)^2$ for $d_\parallel = 2$. The equivalent of the perturbation expansion in (3.9a) is also presented by Kosmas[5] for $\epsilon \approx 0^+$. Renormalization constants and fixed points arising from the perturbation expansion (3.9a) are given in the Appendix.

The RG calculations of Kosmas[5] do not describe the double crossover but only the limit of large or vanishing values of $z_2^0$ and $z_s^0$. An exact description of multiple interaction crossover is a nontrivial generalization of the single interaction crossover dependence.[19,21,22] Fortunately, the RG analysis for a polymer with excluded volume and interacting with a penetrable surface is mathematically *identical* with order $\epsilon$ to the combined description of excluded volume and hydrodynamic interactions for both the Kirkwood–Riseman and Rouse–Zimm models of polymer dynamics, problems which are described by Wang et al.[23] (see Appendix). It is only necessary to transcribe the hydrodynamic interaction labels to surface interaction labels to utilize the results obtained from the hydrodynamic theory. For this reason our discussion of the RG analysis is confined to the Appendix and is very brief.

Combining (3.9a) and (3.9b) enables $\langle \mathbf{R}_\perp{}^2 \rangle$ to be written to first order in $\epsilon$ as

$$\langle \mathbf{R}_\perp{}^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_\mathrm{f}(1 + z_s^0) + \mathcal{O}(\epsilon^2) \tag{3.10}$$

where $\langle \mathbf{R}^2 \rangle_\mathrm{f}$ is the perturbed free chain value defined in (3.9b). Using the RG analysis summarized in the Appendix transforms (3.10) into

$$\langle \mathbf{R}_\perp{}^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_\mathrm{f}[1 + u_s(z_2^0, z_s^0)] + \mathcal{O}(\epsilon^2) \tag{3.11}$$

which is analogous to (3.5a) to first order in $\epsilon$ except that

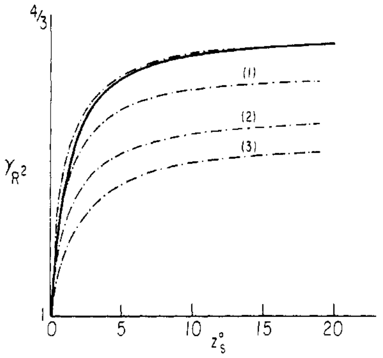

**Figure 1.** Expansion of the mean-square end-to-end vector distance of a polymer terminally attached to a penetrable interacting surface ($d = 3$, $d_\parallel = 2$) relative to that of a free chain $\gamma_{R^2} \equiv \langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_f$. Solid dark line denotes the exact crossover function for Gaussian chains ($z_2^0 = 0$), and the broken lines denote the first order in $\epsilon$ RG prediction given in (3.14). Numbered curves denote the crossover curves from (3.14) for increasingly large excluded volume interaction: (1) $z_2^0 = 0.125$; (2) $z_2^0 = 1$; (3) $z_2^0 = 10$. The unnumbered dash-dot line is for a Gaussian chain $z_2^0 = 0$. The main effect of the excluded volume interaction for $z_2^0 \approx (0.1)$ is to decrease the asymptotic value of $\gamma_{R^2}$. When $z_2^0 \geq \mathcal{O}(1)$, the asymptotic value of $\gamma_{R^2}$ for large $z_s^0$ is roughly constant, but the rate at which this limit is reached with increasing $z_s^0$ is diminished by excluded volume.

$\langle \mathbf{R}^2 \rangle_{0,f}$ is replaced by the perturbed value $\langle \mathbf{R}^2 \rangle_f$, and the coupling constant $u_s = u_s^* \lambda_s$ in (3.5a) is replaced by its analogue with excluded volume as defined in (A.8b) by

$$u_s(z_2^0,z_s^0) = u_s^*(\lambda_2) \times [z_s^0(1 - \lambda_2)^{1/4}/u_s^*(\lambda_2)]/[1 + z_s^0(1 - \lambda_2)^{1/4}/u_s^*(\lambda_2)] \qquad (3.12a)$$

$$u_s^*(\lambda_2) = (\epsilon/2)(3\lambda_2/4)/[1 - (1 - \lambda_2)^{3/4}] \qquad (3.12b)$$

The crossover function in (3.12a) exhibits some interesting qualitative features. First, the effective excluded-volume-dependent dimensionless polymer–surface interaction parameter $\hat{z}_s = z_s^0(1 - \lambda_2)^{1/4}$ is *reduced* by an increase in the excluded volume interaction. For large $z_2^0$ we have $\hat{z}_s \propto z_s^0(z_2^0)^{-1/4}$, so that the crossover exponent $\phi_s$, defined by $\hat{z}_s \propto n_0^{\phi_s}$, is equal to $\phi_s = 3\epsilon/8 + \mathcal{O}(\epsilon^2)$ (see ref 9). Also, the limiting value of $u_s^*(\lambda_2)$ in the large $z_2^0$ limit is reduced by an increased excluded volume interaction, and this point is discussed in detail in the next subsection.

It is straightforward to show that *any* equilibrium radial property $Q$, scaling as the polymer radius to a power $p$, for a polymer attached to a penetrable interacting surface behaves to first order in $\epsilon$ as

$$Q(\text{surface}) = Q_f[1 + A_Q u_s(z_2^0,z_s^0)] + \mathcal{O}(\epsilon^2) \qquad (3.12c)$$

where $Q_f$ is the perturbed (i.e., excluded volume dependent) magnitude of the property $Q$ for a polymer in free space and where $A_Q$ is first order in the $z_s^0$ expansion coefficient [$A_Q = 1$ in (3.10)] for the property $Q$ as calculated with the polymer–surface interaction perturbation theory for a Gaussian chain interacting with the surface. This makes the calculation to order $\epsilon$ of polymer properties for a surface-interacting polymer rather straightforward. Because a repulsive surface interaction expands the molecular dimensions, the constant $A_Q$ is generally positive for $p > 0$. The crossover function $u_s(z_2^0,z_s^0)$ of (3.12) is reduced by an increase in the excluded volume interaction, hence the ratio $Q(\text{surface})/Q_f$ is *always* reduced by increasingly repulsive excluded volume interactions. This amounts then to a general principle.

**D. Comparison between Penetrable and Impenetrable Surface Models.** It is of interest to compare the double-crossover dependence of $\langle \mathbf{R}_\perp{}^2 \rangle$ on $z_s^0$ and $z_2^0$ for a penetrable surface with the calculations of Nemirovsky and Freed[6] for the impenetrable interaction surface and with lattice data for the impenetrable interacting surface. The values of $\langle \mathbf{R}_\perp{}^2 \rangle$ are identical (to all orders in $z_s^0$) for a *Gaussian* chain terminally attached to either penetrable or impenetrable surfaces.[7] This should no longer be the case when excluded volume is incorporated into the theory except in the limit of very repulsive surface interactions where the polymer should no longer be capable of distinguishing a penetrable from an impenetrable surface. To make the comparisons more quantitative we rewrite (3.11) in the equivalent form (see below) to order $\epsilon$ as

**Table I**
**Dimensionless Ratio $\gamma_{R^2} = \langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_f$ for Limiting Values of the Polymer–Polymer and Polymer–Surface Interaction**

| | $\gamma_{R^2}$ (theory) | $\gamma_{R^2}$ (lattice data) |
|---|---|---|
| Penetrable Surface ($d = 3$, $d_\parallel = 2$) | | |
| $z_s^0 \rightarrow \infty$, $z_2^0 \rightarrow \infty$ | 1.20[a] | |
| $z_s^0 \rightarrow \infty$, $z_2^0 \rightarrow 0$ | 1.33[a] | |
| $z_s^0 \rightarrow 0$, $z_2^0 \rightarrow \infty$ | 1[a] | |
| $z_s^0 \rightarrow 0$, $z_2^0 \rightarrow 0$ | 1[a] | |
| Impenetrable Surface[b] ($d = 3$, $d_\parallel = 2$) | | |
| $z_s^0 \rightarrow \infty$, $z_2^0 \rightarrow \infty$ | 1.18[b] | 1.2[c] |
| $z_s^0 \rightarrow \infty$, $z_2^0 \rightarrow 0$ | 1.33[b] | 1.33[d] |
| $z_s^0 \rightarrow 0$, $z_2^0 \rightarrow \infty$ | 1.07[b] | |
| $z_s^0 \rightarrow 0$, $z_2^0 \rightarrow 0$ | 1.00[b] | |

[a] Equation B.7. [b] References 6 and 7. [c] Reference 38. [d] Reference 1.

$$\langle \mathbf{R}_\perp{}^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_f/[1 - u_s(z_2^0,z_s^0)] + \mathcal{O}(\epsilon^2) \qquad (3.13a)$$

which in the absence of excluded volume *exactly* recovers (3.5c) for $z_s^0 \rightarrow \infty$. Moreover, Figure 1 compares (3.13a) with the exact solution for Gaussian chains ($z_2^0 = 0$). The $z_s^0 \gg 1$ asymptotic limit of (3.13a) for $d_\perp = 1$ yields

$$\langle \mathbf{R}_\perp{}^2 \rangle \sim (\langle \mathbf{R}_2 \rangle_{0,f}/d)[2 - 1/z_s^0 + \mathcal{O}(z_s^0)^2] \qquad z_s^0 \gg 1, \; z_2^0 = 0 \qquad (3.13b)$$

which, as shown in Figure 1, is the *exact* limiting behavior of $\langle \mathbf{R}_\perp{}^2 \rangle$ given in eq 3.12 of ref 7. Our general expression for $\langle \mathbf{R}^2 \rangle$ for an interacting surface is then obtained from (3.3a), (3.5e), and (3.13a) as

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_f [d_\parallel + d_\perp/(1 - u_s)]/d + \mathcal{O}(\epsilon^2), \qquad d_\parallel = 2 \qquad (3.14)$$

where $u_s(z_s^0,z_2^0)$ is defined by (3.12a). Equation 3.13a is strictly correct only to order $\epsilon$, and the rearrangement from (3.5a) to (3.13a) is motivated by the exactly known limits for Gaussian chains. The first order in the $\epsilon$-crossover scaling function (3.13a) is dramatically improved by this maneuver, as can be seen by comparing Figure 1 with Figure 2 of ref 7.

Table I compares limiting values of the ratio $\gamma_{R^2} \equiv \langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_f$ for the penetrable and impenetrable surface as obtained from (3.13) and from ref 9, respectively. Only small differences are found, as expected, between the penetrable and impenetrable surface values of $\gamma_{R^2}$ for large $z_2^0$ and $z_s^0$. This slight discrepancy is almost certainly due to the different perturbative methods on which the penetrable and impenetrable surface calculations are based (see below). For $z_s^0 \rightarrow 0$, on the other hand, Table I shows that $\gamma_{R^2}$ does not approach unity for an impenetrable surface as it does for the penetrable surface (by definition!). Apparently the presence of an impenetrable surface generates an effective "repulsive" interaction for chains with excluded volume. Wang et al.[8] consider a variably penetrable surface for the special case of $d_\perp = 1$ and Gaussian chains, and we plan to include a parameter accounting for "penetrability" in future work.

More subtle aspects of the influence of polymer–polymer excluded volume on the dimensions of a surface-interacting polymer are present in Figure 1. A slight amount of excluded volume interaction reduces the asymptotic value of $\gamma_{R^2}$ substantially, but larger values of the excluded volume interaction have the predominant effect of slowing the rate at which the asymptotic limit is reached with an increasing surface repulsion. The physical origin of the effect observed in Figure 1 is rather obvious. An expansion of the chain reduces the coil density, the probability of the chain encountering the surface, and thus the influence of the repulsive surface on the polymer dimensions. A similar splitting pattern in the scaling functions is found for hydrodynamic polymer properties in good solvents, and this effect is discussed by Wang et al.[24] (see also Appendix).

The relatively simple crossover dependence in (3.13) is to be contrasted with the very complicated crossover description of $\gamma_{R^2}$ in the theory of Nemirovsky and Freed[6] for the impenetrable surface. This difference arises because Nemirovsky and Freed[6] treat the surface interaction and the excluded volume interactions "undemocratically" since they solve exactly the Gaussian surface interaction problem as their unperturbed state and then incorporate the excluded volume perturbatively. This simplifies their RG analysis since there is only a single perturbative parameter, but this savings is at the expense of much more difficult perturbation calculations and a much more complicated description of the crossover dependence on both interactions.

## IV. Qualitative Description of Attractive Interactions

**A. Problems Arising in the Treatment of Attractive Interactions.** The theoretical description of polymers with attractive interactions is a much more difficult task than the treatment of repulsive interactions. Several complicating factors of mathematical and physical origin arise and are described to delineate the situations to which our calculations are generally applicable.

First of all, the Gell-Mann–Low RG method is restricted to arbitrary positive and very small negative values of $z_2^0$ and $z_s^0$. This matter is discussed in ref 7, but it is quite apparent from the definition of the functions $\lambda_2$ and $\lambda_s$ in (3.5b) and (3.6b) which evidently become singular as $z_2^0 \to -u_2^*$ and $z_s^0 \to -u_s^*$, respectively. Some insight into the breakdown of the RG theory in the range of attractive interactions emerges from the exact ($d_\parallel = 0$) solution for the Gaussian chain polymer–surface interaction model. The end-vector distribution function is dominated for $z_s^0 \lesssim -u_s^*$ by the leading term in its eigenfunction expansion.[2,7] This type of ground-state-dominant approximation is also believed to determine the physics of free polymers with attractive polymer–polymer interactions in the contracted "globular" state.[25,26] A description of attractive interactions ($z_2^0 \lesssim -u_2^*$, $z_s^0 \lesssim -u_s^*$) requires a perturbative expansion about the limiting collapsed or adsorbed states rather than the Gaussian coil.[27]

The theoretical treatment of strong attractive interactions is fraught with difficulties of a physical origin in addition to the mathematical difficulty in treating this regime by using the RG method. The most serious of these difficulties arises because a polymer confined to a smaller region of space than a free Gaussian coil has a much higher probability of self-intersection with itself. This is reflected by the relevance of interactions that otherwise would be unimportant for the free weakly interacting chain in three dimensions. For example, when a polymer is collapsed into itself from attractive polymer–polymer interactions or when a polymer is adsorbed onto a two-dimensional surface, there are, in principle, an infinity of relevant excluded volume interaction parameters in the continuum-type models with $\delta$-function interactions.[7,12] Furthermore, short-range correlations in collapsed polymers are generally not the same as in a free chain. This implies that the Kuhn length, which models the short-range interactions, should be affected by the attractive surface interactions.

Finally, there are instances in which the continuum model (2.2) and (2.3) of interacting polymers gives unphysical results for attractive interactions even though the mathematical model may be solved exactly.[1,27] For example, a Gaussian chain with an attractive polymer–surface interactions is found to give[7]

$$\langle \mathbf{R}_\perp{}^2 \rangle \sim (d_\perp \langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}/d)|z_s{}^0 \Gamma(\epsilon_\perp/2)|^{-2/\epsilon_\perp} \qquad z_s{}^0 \lesssim -u_s^* \tag{4.1}$$

so that for large $[|\beta_s{}^0/l^{d_\perp}| \sim 0(1)]$, i.e., highly attractive polymer–surface interactions, $\langle \mathbf{R}^2 \rangle$ approaches[27] [see (3.3)]

$$\langle \mathbf{R}^2 \rangle \to d_\parallel \langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}/d \langle \mathbf{R}_\perp{}^2 \rangle \to 0 \tag{4.2}$$

instead of the correct $d_\parallel$-dimensional random walk result of

$$\langle \mathbf{R}^2 \rangle \to \langle \mathbf{R}^2 \rangle_{0,\mathrm{f}} \tag{4.3}$$

Heuristically, this difficulty arises because the dimensionality of space that the polymer "senses" is a function of the surface interaction.[7] The naive factorization of $G$ into $G_\parallel$ and $G_\perp$ [see (3.3b)], which the model indicates, is not physically correct for highly attractive interactions and reflects a breakdown of the continuum Gaussian model description of polymer adsorption.[27] The lattice model calculations of Rubin[1] do not suffer from this difficulty of the Gaussian continuum model, and Rubin[1] finds that $\langle \mathbf{R}_\parallel{}^2 \rangle$ is a function of the surface interaction in the attractive interaction regime, so that (4.3) is satisfied for strong adsorption. On the other hand, Rubin's calculations indicate that the continuum model should be a good approximation[27] in the "weak adsorption" limit where $|\beta_s{}^0/l^{d_\perp}| \ll 1$ in accordance with the arguments of de Gennes.[2] Weak adsorption corresponds to a temperature $T$ close to the adsorption $\Theta$-point $\theta_A$ where $\beta_s{}^0$ vanishes.[9]

Similar difficulties with the usual continuum model of Gaussian polymers occur generally for geometrically confined polymers. For example, Dolan and Edwards[28] calculate the end-vector distribution function of a terminally attached Gaussian polymer between two parallel repulsive plates. It is then readily found ($d_\perp = 1$) from their work that

$$\begin{aligned}\langle \mathbf{R}_\perp{}^2 \rangle_0 = (\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}/d)(k^2/2)[1 - 2(k/\pi)^2] + \\ \mathcal{O}\{\exp[-3(\pi/k)^2/2]\}, \qquad k = (d/\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}})^{1/2}\mathcal{L}\end{aligned} \tag{4.4}$$

where $\mathcal{L}$ is the plate separation. For small plate separations ($k \to 0$) eq 4.4 again yields (4.2) instead of the correct (4.3). Application of the continuum model is thus restricted to weak compression where $k \sim \mathcal{O}(1)$. There is evidently a need for careful analysis of the passage to the continuum limit when there are strong attractive polymer–surface interactions or when there is confinement to small regions of space.

**B. Weakly Attractive Interactions and the Adsorption Threshold.** A limited extension of the RG theory can be made into the regime of weak attractive interactions ($z_s{}^0 \gtrsim -u_2^*$) by using arguments first presented for polymer–polymer excluded volume interactions.[12] The extension to weakly attractive polymer–surface interactions

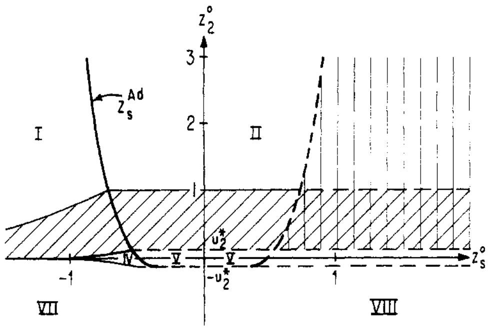

**Figure 2.** States of the surface-interacting polymer with excluded volume interactions.[29] Region I denotes the state of adsorbed swollen chains, which is separated from region II by a dark line indicating the adsorption threshold [see (4.6)]. Region II corresponds to desorbed swollen polymers with a weak surface interaction. Vertical lines denote the crossover region separating region II from the depletion regime at high $z_s^0$ where the polymer is strongly repelled from the surface. The transition from region II to the depletion regime [$z_s^0 \sim \mathcal{O}(5)$] is rather broad (see Figure 1). Slanted lines indicate the crossover regime separating near-Gaussian coils $|z_2^0| \leq u_2^*$ from swollen chains $z_2^0 \geq \mathcal{O}(1)$. Region IV consists of adsorbed near-Gaussian coils, while region V has desorbed near-Gaussian coils. Regions III and VI for depleted swollen and Gaussian coils, respectively, are not indicated since these domains occur at large $z_s^0$ (see Figure 1). There are also regions VII and VIII separating adsorbed and desorbed globules, but we can give no indication of the separation between these domains.

involves letting $z_s^0$ be negative in (3.13a). We confine attention to $\langle \mathbf{R}_\perp^2 \rangle$ under the restriction of weak adsorption. A rearrangement of (3.13a) using the definition of $u_s$ from (3.12a) gives

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp \langle \mathbf{R}^2 \rangle_f / d)[1 + \hat{\Delta}(z_2^0)] / \{1 + \hat{\Delta}(z_2^0)[1 - u_s^*(\lambda_2)]\} \quad (4.5a)$$

$$\hat{\Delta}(z_2^0) \equiv z_s^0 (1 + z_2^0/u_2^*)^{-1/4} / u_s^*(\lambda_2) \quad (4.5b)$$

where the quantity $\hat{\Delta}$ is introduced for notational compactness. Evidently (4.5a) is unphysical for $\hat{\Delta} \leq -1$ since this makes $\langle \mathbf{R}_\perp^2 \rangle$ negative. The limit $\hat{\Delta} \to -1^+$ defines the "adsorption threshold" where $\langle \mathbf{R}_\perp^2 \rangle \to 0^+$ (see Figure 2 of ref 7) as well as a critical value of $z_s^0$.

$$z_s^0(\text{adsorption threshold}) \equiv z_s^{Ad} = -u_s^*(\lambda_2)(1 + z_2^0/u_2^*)^{1/4} + \mathcal{O}(\epsilon^2) \quad (4.6)$$

A plot of $z_s^{Ad}$ vs. $z_2^0$ is given in Figure 2, where $z_s^{Ad}$ separates[29] regions I and II corresponding to adsorbed and desorbed swollen polymer chains, respectively. The curve $z_s^{Ad}$ also separates regions IV and V for adsorbed and desorbed near-Gaussian coils, respectively.

**C. Surface Depletion.** An increase of the repulsive polymer–surface interaction leads to swelling of the polymer chain to an extent that decreases with increasing repulsive excluded volume interaction. (See subsection A and Figure 1.) There is a gradual crossover from the adsorption Θ-point, where the polymer–surface interaction vanishes, to the limiting absorbing boundary conditions for $\hat{\Delta} \geq \mathcal{O}(5)$ where the surface layer is "depleted" of polymer.[30] The surface interaction begins to saturate (see Figure 1) for $\hat{\Delta} \geq \mathcal{O}(1)$, and there is substantial leveling off of the crossover curves for $\hat{\Delta} \sim \mathcal{O}(5)$ where $u_s \approx u_s^*$.

**D. Rough Description of Strong Surface Adsorption.** Despite the numerous difficulties in describing the regime of strong attractive interactions by using the Gaussian chain model and idealized δ-function pseudopotential interactions, we expect that these continuum coarse-grained models should describe qualitative aspects of the collapse of the polymer into itself or onto a surface.

Reference 7 shows that the end-to-end vector distribution function for Gaussian chains interacting with a $d_\parallel$-dimensional surface through an attractive ($z_s^0 \lesssim -u_s^*$) δ-function interaction is described accurately by the ground-state-dominant propagator $G_\perp^{gsd}$ given by[7]

$$G_\perp^{gsd} \propto \hat{r}_\perp^{\epsilon_\perp/2} K_{\epsilon_\perp/2}(\hat{r}_\perp) \qquad z_s^0 \lesssim -u_s^* \quad (4.7a)$$

where $K_{\epsilon_\perp/2}$ is a modified Bessel function and where $\mathbf{r}_\perp$ is in the reduced units $\hat{r}_\perp$ defined as[7]

$$\hat{r}_\perp = |\hat{\mathbf{r}}_\perp| = (\langle \mathbf{R}^2 \rangle / \xi_\perp^2)^{1/2} |\mathbf{r}_\perp| \quad (4.7b)$$

$$\xi_\perp^2 = |z_s^0 \Gamma(\epsilon_\perp/2)|^{-2/\epsilon_\perp} (\langle \mathbf{R}^2 \rangle_{0,f}/2) \quad (4.7c)$$

The scale $\xi_\perp$ is a surface correlation length (see also ref 2) which characterizes the average extension of the polymer coil from the surface for $z_s^0 < -u_s^*$. This can be seen by comparing (4.1) and (4.7c), where we find

$$\xi_\perp^2 = (d/d_\perp)(\langle \mathbf{R}_\perp^2 \rangle / 2) \quad (4.7d)$$

Equation 4.7 reduces for $d_\perp = 1$ to the ground-state-dominant solution given by de Gennes[2,21] for an attractive impenetrable surface, so that our qualitative discussion applies equally well for both penetrable and impenetrable surfaces ($d_\perp = 1$). The factor of $|z_s^0 \Gamma(\epsilon_\perp/2)|^{-2/\epsilon_\perp}$ in (4.7c) scales from (2.2d) as $1/n_0$, and hence (4.7c) implies

$$\xi_\perp^2 \sim l^2 \quad (4.8a)$$

where the proportionality constant is governed by the temperature-sensitive term $|\beta_s^0 / l^{d_\perp}|^{-2/\epsilon_\perp}$. When $|\beta_s^0 / l^{d_\perp}|^{-2/\epsilon_\perp}$ is on the order of unity (strong surface adsorption), the entire polymer is on average confined within a step-length distance from the surface. In the limit $z_s^0 \to -1/\Gamma(\epsilon_\perp/2) \approx -u_s^*$ the surface correlation length grows very rapidly and (4.7c) becomes

$$\xi_\perp^2 \to \langle \mathbf{R}^2 \rangle / 2 \qquad z_s^0 \to -u_s^* \quad (4.8b)$$

so that the dimensions of the coil normal to the surface are comparable to that of a free Gaussian coil. The limit $z_s^0 \to -u_s^*$ defines the adsorption threshold for Gaussian chains, and it is not meaningful[7,27] to apply the ground-state-dominant theory for $z_s^0 \to -u_s^*$.

The treatment of attractive polymer–surface interactions in conjunction with a repulsive or small attractive excluded volume interaction follows in the same manner as for repulsive polymer–surface interactions, except that the $G_\perp^{gsd}$ approximate propagator replaces the $G_\perp^0$ propagator of a free chain in the perturbation expansion [see (3.2) and (3.3)]. An important property of the adsorbed polymer [$z_s^0 \ll -u_s^*$] is that $G_\perp^{gsd}$ is independent of the contour distance variable because $\xi_\perp^2$ in (4.7c) is *independent of* $n_0$. The same is true in Dolan and Edward's parallel plates propagator for small plate separation[28] where $G_\perp$(parallel plates) is a function of $R_\perp/\mathcal{L}$. A perturbation expansion using the ground-state-dominant approximation or the leading term in $G_\perp$(parallel plates) leads to an expansion in which the poles in the excluded volume perturbation expansion are found to involve the variable $\epsilon' = 4 - d_\parallel$, where $d_\parallel$ is the surface dimension rather than $\epsilon = 4 - d$ for nonattractive or unconfined cases. A complete discussion of the perturbative expansion in excluded volume for the ground-state-dominant theory and parallel plates is avoided because of the potential inaccuracy of the starting Gaussian chain model of adsorbed polymers and the possible need for corrections to the leading ground-state-dominant term in the expansion of $G_\perp$.[31] Rather, we now present a general scaling argument demonstrating the qualitative effects of the combined excluded volume and attractive polymer–surface interactions.

It is convenient to first factor the $\delta$-function interaction in the Hamiltonian (2.3a) into parallel and perpendicular contributions

$$\delta[\mathbf{r}(x) - \mathbf{r}(x')] = \delta[\mathbf{r}_{\parallel}(x) - \mathbf{r}_{\parallel}(x')]\delta[\mathbf{r}_{\perp}(x) - \mathbf{r}_{\perp}(x')] \tag{4.9a}$$

Introducing the $\hat{r}$ units of (4.7b) appropriate to the $G^{\mathrm{gsd}}(\hat{r})$ distribution ($z_{\mathrm{s}}^0 \lesssim -u_{\mathrm{s}}^*$) gives

$$H = z_{2\mathrm{A}}{}^0 \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}x' \; \delta[\mathbf{r}_{\parallel}(x) - \mathbf{r}_{\parallel}(x')]\delta[\hat{\mathbf{r}}_{\perp}(x) - \hat{\mathbf{r}}_{\perp}(x')](2\pi)^{d/2} \tag{4.9b}$$

where the modified dimensionless excluded volume variable $z_{2\mathrm{A}}{}^0$ appearing in (4.9) is

$$z_{2\mathrm{A}}{}^0 = (z_2{}^0/2)(\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}/\xi_{\perp}{}^2)^{d_{\perp}/2} \tag{4.10a}$$

Alternatively, introducing (4.7c) into (4.10a) produces

$$z_{2\mathrm{A}}{}^0 = (z_2{}^0/2)|z_{\mathrm{s}}{}^0\Gamma(\epsilon_{\perp}/2)|^{d_{\perp}/\epsilon_{\perp}} \tag{4.10b}$$

The modified excluded volume interaction $z_{2\mathrm{A}}{}^0$ has the limiting scaling behavior from (4.6) of

$$z_{2\mathrm{A}}{}^0 = z_2{}^0 n^{-d_{\perp}/2} \sim n^{\epsilon'/2}, \qquad \epsilon' = 4 - d_{\parallel},\ |\beta_{\mathrm{s}}{}^0/l^{d_{\perp}}| \sim \mathcal{O}(1) \tag{4.11}$$

Scaling the parallel plate propagator $G(\mathbf{r}_{\parallel}, R_{\perp}/\mathcal{L})$ as in (4.9b) leads to the same type of modified excluded volume interaction $z_{2\mathrm{A}}{}^0(\mathcal{L})$ where $\mathcal{L}$ replaces $\xi$ in (4.10a) (see ref 7). Confinement of the polymer due to a physical boundary and an attractive interaction are closely analogous.[31]

The scaling argument in (4.9)–(4.11) is sufficient for the discussion of many qualitative aspects of polymer adsorption when excluded volume is also present. First, an increased polymer–surface interaction produces an increase in the excluded volume interaction $z_{2\mathrm{A}}{}^0$. Basically this occurs because the excluded volume effect is more pronounced when the dimension is lower, and an increase of the attractive polymer–surface interaction in effect confines the polymer to a lower dimension. When there is also a small repulsive excluded volume interaction, we expect a large swelling of the chain upon adsorption onto the attractive surface. A small attractive polymer–polymer interaction should make the polymer coil contract upon adsorption onto the surface because the polymer–surface interaction amplifies the magnitude of the excluded volume interaction in the attractive $z_{\mathrm{s}}{}^0$ interaction regime. These qualitative features are observed in Monte Carlo simulations.[32]

In the absence of a polymer–surface interaction, the incipient coil collapse into itself is roughly specified by the condition[12]

$$z_2{}^0(\text{self-collapse}) \approx z_2{}^c \approx -u_2^* \tag{4.12}$$

which is determined in a completely analogous way as that leading to (4.6). We now generalize this condition for self-collapse to adsorbed polymers using the scaling arguments above. The perturbation expansion in excluded volume for strong polymer–surface attraction in the ground-state-dominant mode approximation leads to an expansion in $z_{2\mathrm{A}}{}^0$ with formal poles in $\epsilon'$. Although this approach is limited to weak adsorption,[27] it *suggests* that the collapse condition should be similar to that of a free chain and thus of the form

$$z_{2\mathrm{A}}{}^0(\text{self-collapse}) \equiv z_{2\mathrm{A}}{}^c \approx -u_2^*(d_{\parallel}) \tag{4.13a}$$

Combining (4.10a) with (4.13a) gives the rough collapse condition for adsorbed chains $z_2{}^c$ as

$$z_2{}^c(\langle \mathbf{R}^2 \rangle_{0,\mathrm{f}}/\xi_{\perp}{}^2)^{d_{\perp}/2} \approx z_2{}^c|z_{\mathrm{s}}{}^0\Gamma(\epsilon_{\perp}/2)|^{d_{\perp}/\epsilon_{\perp}}2^{d_{\perp}/2} \approx u_2^*(d_{\parallel}) \tag{4.13b}$$

Rearranging (4.13b) yields

$$z_2{}^c = -c|z_{\mathrm{s}}{}^0\Gamma(\epsilon_{\perp}/2)|^{-d_{\perp}/\epsilon_{\perp}} \tag{4.13c}$$

where $c$ is a positive constant. When $z_{\mathrm{s}}{}^0$ is large and attractive, $z_2{}^c$ approaches zero as schematically depicted in Figure 2. This picture of polymer adsorption, presented by (4.13c), suggests that adsorbed Gaussian polymers at infinite dilution should *exist* over a rather narrow temperature range and that the dimensions of adsorbed polymers should change rather sharply upon passing through the Flory $\Theta$-temperature of the adsorbed polymer. The $\Theta$-temperature of the adsorbed polymer is, of course, not in general the same as that of the free polymer because $\beta_2{}^0(d_{\parallel}) \neq \beta_2{}^0(d)$.

Neutral or weakly repulsive polymer–surface interactions combined with strong attractive polymer–polymer interactions should have little influence on polymer dimensions, since the polymer can simply *move off the surface* to become a free polymer chain in solution aside from the point of attachment. This argument implies that the condition for incipient self-collapse of the chain to a globule (eq 4.12a) should be roughly the same as for a free chain.

We cannot even speculate on the location of the line separating the desorbed-globule and absorbed-globule states that is likely to exist for strong attractive excluded volume and polymer–surface interactions. It might be expected that an increasingly attractive polymer–surface interaction would be necessary to overcome attractive polymer–polymer interactions. Figure 2, however, indicates that the adsorption threshold from (4.6) for weakly attractive polymer–polymer and polymer–surface interactions approaches the adsorption $\Theta$-point $z_{\mathrm{s}}{}^0 = 0$ as the binary interaction approaches $z_2{}^0 \rightarrow -u_{\mathrm{s}}^*$ from above. Hence, attractive polymer–polymer interactions probably *favor* adsorption onto the surface. Further work is needed in elucidating the states of attractive surface-interacting polymers, and the discussion in this speculative subsection simply sketches out the phenomena we would like to describe using more adequate theoretical methods.

## V. Conclusions

The renormalization group method is applied to the description of a polymer with excluded volume interacting with a penetrable surface. The prediction, that the mean-square end-to-end vector distances $\langle \mathbf{R}^2 \rangle$ are identical for Gaussian chains at penetrable and impenetrable surfaces, persists for repulsive surfaces when excluded volume is incorporated into the theory, but important differences arise in the limit of vanishing surface interactions. The basic conclusion of our calculations for repulsive polymer–surface interactions is that an increase in the repulsive excluded volume interaction has the effect of diminishing the effect of the repulsive surface interaction on the dimension of the surface-interacting polymer relative to its dimensions free of the presence of an interacting surface. We believe this effect is true regardless of whether the surface is penetrable or impenetrable.

A similar effect is found elsewhere for the expansion of chain dimensions within a block copolymer where one of the blocks is then analogous to the surface and where the interblock interaction is analogous to the polymer–surface interaction.[9,33,34] An increase of the excluded volume interaction within a block of an AB block copolymer has the effect[9,33-35] of diminishing the expansion of the block, due to the interblock interaction, relative to the dimensions for the block unconfined to the copolymer. This basic effect has an obvious physical interpretation: the greater the block expands with excluded volume, the lower the polymer density becomes, so that there is a decreased probability of the block encountering the other block.

The same general principle is also found to be important in the description of polymer hydrodynamics. An extension of the results in the Appendix for the Kirkwood–Riseman and Rouse–Zimm theories[23] to second order in $\epsilon$ indicates that the scaling functions for hydrodynamic properties are split in a similar fashion to the surface interaction crossover curves in Figure 1. The effect is particularly dramatic in this case since the exponents characterizing the mean hydrodynamic dimensions of the polymer may then depend on the hydrodynamic and excluded volume interactions. The origin of this physical effect is similar to the surface interaction and block copolymer problems. An expansion of the chain lowers the chain density, which in turn reduces the extent of hydrodynamic interaction.

*Attractive* polymer–surface interactions lead to very different behavior since an increase in the attractive polymer–surface interactions tends to confine the polymer to the adsorbing surface. The lowering of the effective dimension sensed by the polymer through a surface attraction greatly increases the excluded volume interactions. When the excluded volume interaction is repulsive, this amplification of excluded volume effects makes the polymer swell greatly along the surface, while even a slight attractive interaction should make the coil "bead up" rather than "wet" the surface.

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## Appendix A. Renormalization Group Analysis and Renormalization Group Equation

Dimensionless coupling constants $u_s^0$ and $u_2^0$ for the polymer–surface and excluded volume interactions, respectively, are defined ($d_{\parallel} = 2$) through

$$z_s^0 = u_s^0(2\pi N/L)^{\epsilon/2} \qquad (A.1a)$$

$$z_2^0 = u_2^0(2\pi N/L)^{\epsilon/2} \qquad (A.1b)$$

where $L$ is an intermediate model variable having the dimensions of length. Renormalization constants are then defined and determined from (A.1a) and (A.1b) and (3.8) as

$$u_s^0 = u_s Z_{u_s}$$

$$Z_{u_s} = 1 + 2u_s/\epsilon + 2u_2/\epsilon + \mathcal{O}(u_s^2, u_2 u_s, u_2^2) \qquad (A.2a)$$

$$u_2^0 = u_s Z_{u_2}, \qquad Z_{u_2} = 1 + 8u_2/\epsilon + \mathcal{O}(u_2^2) \qquad (A.2b)$$

$$N^0 = NZ_N^{-1}, \qquad Z_N = 1 + 2u_2/\epsilon + \mathcal{O}(u_2^2) \qquad (A.2c)$$

where we employ the minimal subtraction scheme in which the $Z$'s remove all formal singularities in $\epsilon$ from the renormalized perturbation expansions in $u_s$, $u_2$, and N. The renormalizability of the theory with both interactions is assumed.

The Gell–Mann–Low $\beta$-functions are defined and are calculated to order $\epsilon$ from (A.2a) and (A.2b) as

$$\beta_2 = L(\partial/\partial L)u_2 = (\epsilon/2)u_2(1 - 8u_2/\epsilon) \qquad (A.3a)$$

$$\beta_s = L(\partial/\partial L)u_s = (\epsilon/2)u_s(1 - 2u_s/\epsilon - 2u_2/\epsilon) \qquad (A.3b)$$

The fixed points $(u_2^*, u_s^*)$ correspond to the zeros of $\beta_2$ and $\beta_s$ and are computed from (A.3) as

$$(u_2^*, u_s^*):\ (0,0),\ (0,\epsilon/2),\ (0,\epsilon/8),\ (\epsilon/8, 3\epsilon/8) \qquad (A.4)$$

These fixed points are the same as those determined previously by Kosmas[5] except that Kosmas's definition[5,37] of $u_2^*$ differs from our convention by a factor of 2. Calculations to first order in $\epsilon$ elsewhere indicate that the $\beta$-function for the hydrodynamic interaction in both the Kirkwood–Risemand and Rouse–Zimm theories is equal to[23]

$$\beta_H = L(\partial/\partial L)u_H^0 = (\epsilon/2)u_H(1 - 2u_H/\epsilon - 2u_2/\epsilon) \qquad (A.3c)$$

which is identical with (A.3b) aside from a change of labels on the interactions.

The scaling function for $\langle \mathbf{R}_\perp^2 \rangle$ follows from (2.2) and (3.1) to have the form

$$\langle \mathbf{R}_\perp^2 \rangle = f(\beta_2^0, \beta_s^0, N_0) \qquad (A.5a)$$

where $f$ is a general scaling function to be determined below. Equation A.5a is rewritten in terms of the RG coupling constants as

$$\langle \mathbf{R}_\perp^2 \rangle = f(u_2^0 L^{-\epsilon/2}, u_s^0 L^{-\epsilon/2}, 2\pi N_0) \qquad (A.5b)$$

Introducing the definition of the renormalization constants from (A.2) into (A.5b) transforms the latter into

$$\langle \mathbf{R}_\perp^2 \rangle = f(u_2 Z_{u_2} L^{-\epsilon/2}, L^{-\epsilon/2} u_s Z_{u_s}, 2\pi N Z_N^{-1}) \qquad (A.5c)$$

Applying $L\partial/\partial L$ to (A.5c) with the arguments $\beta_2^0$, $\beta_s^0$, and $N_0$ fixed yields the renormalization group equation

$$\left( L\frac{\partial}{\partial L} + \beta_{u_2}\frac{\partial}{\partial u_2} + \beta_s\frac{\partial}{\partial u_2} + \gamma_N N\frac{\partial}{\partial N} \right)_F f = 0 \qquad (A.6)$$

where $\gamma_N = L(\partial \ln Z_N/\partial L)_F$ and where F denotes that the arguments of $f$ in (A.5a) are fixed.

The solution of (A.6) follows the discussion given by Wang et al.[23] and Douglas et al.[34] for the hydrodynamic interaction and block copolymer problems, respectively. In first order in $\epsilon$ the scaling function $f$ is determined by using this analogy as

$$f[L^{-\epsilon/2}\bar{u}_2/(1 - \bar{u}_2),\ L^{-\epsilon/2}\bar{u}_s(1 - \bar{u}_2)^{-1/4}/(1 - \bar{u}_s),\ N(1 - \bar{u}_2)^{1/4}] \qquad (A.5d)$$

$$\bar{u}_2 = u_2/u_2^*, \qquad u_2^* = \epsilon/8 + \mathcal{O}(\epsilon^2) \qquad (A.5e)$$

$$\bar{u}_s = u_s/u_s^*, \qquad u_s^* = (\epsilon/2)(3\lambda_2/4)/[1 - (1 - \lambda_2)^{3/4}] \qquad (A.5f)$$

where $\lambda_2$ is defined in (3.6) and below in (A.8a).

Scaling (A.5d) in the usual fashion[19,21,22] gives the dimensionless scaling variables

$$\zeta = z_2^0/u_2^* = (2\pi N/L)^{\epsilon/2}\bar{u}_2/(1 - \bar{u}_2)^{1-\epsilon/8} \qquad (A.7)$$

$$\zeta_s = z_s^0/u_s^* = (2\pi N/L)^{\epsilon/2}[\bar{u}_s/(1 - \bar{u}_s)](1 - \bar{u}_2)^{-1/4+\epsilon/8} \qquad (A.8)$$

The equality $\zeta = z^0/u^*$ for both types of interactions enables us to reinterpret the $\{z_i^0\}$ as phenomenological RG scaling variables. Inverting (A.7) and (A.8) to determine $u_2$ and $u_s$ as functions of $z_2^0$ and $z_s^0$ yields

$$u_2 = u_2^*(z_2^0/u_2^*)/(1 + z_2^0/u_2^*) + \mathcal{O}(\epsilon^2) = u_2^*\lambda_2 + \mathcal{O}(\epsilon^2) \qquad (A.9a)$$

$$u_s(z_2^0, z_s^0) = u_s^*[(z_s^0/u_s^*)(1 + z_2^0/u_2^*)^{-1/4}]/[(z_s^0/u_s^*) \times (1 + z_2^0/u_2^*)^{-1/4} + 1] \qquad (A.9b)$$

Equation (A.9) is to be substituted into renormalized perturbation expansions in $u_2$ and $u_s$ in order to make the latter expansions consistent with the constraints of the RG equation. The second-order RG analysis is extremely difficult to perform exactly, and an approximation scheme is introduced in Wang et al.[23] and Douglas and Freed[34] to treat this problem. This type of analysis is not needed here.

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$$\gamma_{R^2} = 1 + \lambda_s(\epsilon \approx 0) + \mathcal{O}[\lambda_s^2(\epsilon \approx 0)], \qquad d_\perp = d = 1,\ d_\parallel = 0$$

$$\lambda_s = z_s/[1 + z_s \ln (2\pi N/L_s)]$$

where this limit implies $z_s \equiv u_s$, so that $\gamma_{R^2}$ for very long chains reduces to

$$\gamma_{R^2} = 1 + 1/\ln (2\pi N/L_s), \qquad d_\perp = d = 1, d_\parallel = 0$$

On the other hand, when $z_s^0$ is very small we have $\gamma_{R^2} = 1 + z_s$, so that simple perturbation theory is adequate. Similar log corrections are predicted for ternary interactions [see: Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1985**, *83*, 5293 and references cited in this paper] at $d = 3$ for infinite chains, but Cherayil et al. show that experimental and Monte Carlo data suggest that the ternary interaction is small, so that the simple perturbative description may be more appropriate. Lattice simulations of Gaussian chains in $d = 2$ interacting with a point and in $d = 3$ interacting with a line would provide a simple model for investigating the practical significance of the log corrections.

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