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How Does Surface Roughness Affect Polymer–Surface Interactions?

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ABSTRACT: Many naturally occurring surfaces (cell membranes and organelles, soils and rocks, etc.) are highly irregular, appearing on average "similar" in roughness over a large range of observational scales. The irregularity of such surfaces can often be quantified through the measurement of the fractal dimension d_{fs} of the surface. In three dimensions, values of d_{fs} near 2 correspond to relatively "smooth" surfaces while surfaces having values $d_{fs} \approx 3$ are relatively "rough" and space filling. A simple model is introduced to qualitatively describe the effect of this kind of surface roughness on the properties of surface interacting polymers and comparison is made with recent Monte Carlo data and renormalization group calculations. The model indicates that increasing the surface irregularity (i.e., the fractal dimension d_{fs}) has the effect of enhancing polymer–surface interactions relative to the idealized planar interface. This is a consequence of a greater probability of polymer–surface intersection with increasing roughness. It is also argued that adsorption occurs more readily on fractal surfaces since adsorption then requires a smaller "entropic price". A rough surface may adsorb a polymer when a corresponding smooth surface of the same material will not adsorb. Roughness can thus alter the effective polymer–surface interaction in a fundamental way.

1. Introduction

Numerous studies have been made of polymers interacting with planar interfaces and to a lesser degree more complicated idealized geometries—spheres, cylinders, etc. Recent renormalization group calculations and simulation studies have focused on incorporating excluded volume into the classical random walk models of surface interacting polymers for these simple geometries.[1] Naturally occurring surfaces[2,3] (cell membranes and organelles, soils, colloidal aggregates, etc.), however, tend to be highly irregular and cannot be reasonably modeled by the conventional smooth surface models.

The problem of an irregular adsorbing interface raises important theoretical and practical questions about how the surface roughness is best characterized. Measurement of the "fractal" dimension[2,4] provides a useful zeroth-order measure of "roughness". Pfeifer et al.,[2] for example, have catalogued a diverse group of naturally occurring fractal surfaces and demonstrated the fundamental role of fractal dimension in the characterization of "real" surfaces.

Since the surfaces of many materials can be accurately chracterized by a fractal dimension, we are naturally led to considering models of Gaussian chains interacting with fractal surfaces. Even the simplest models of Gaussian chains interacting with a fractal surface, however, lead to formidable mathematical difficulties. An obvious and familiar example is a diblock copolymer where one block can be considered a fractal surface. Analytic calculations for this system can be obtained by using the renormalization group method in conjunction with an ϵ-expansion.[5] Another important example involves a Gaussian chain interacting with dense random impurities (a fractal dust[4]), which is studied numerically by Baumgartner and Muthukumar[6] and analytically by Thirimulai,[7] Edwards and Muthukumar,[8] and Douglas.[9] A rigorous treatment of a polymer interacting with a fractal surface is complicated by the difficulty in incorporating boundary conditions into the diffusion equation (or equivalent path integral) describing the interacting polymer. At the present stage a combination of model building and Monte Carlo simulation is useful to identify the essential features of the problem.

The aim of the present work is to introduce a simplified but tractable model of polymers interacting with rough (fractal) surfaces. A Gaussian chain interacting with surfaces having continuously variable dimension is solved in previous work and the crux of the "effective surface" (ES) model, discussed here, is to identify the continuously variable surface dimension with the fractal dimension d_{fs} of the rough surface. The ES model presumes that the physics of a polymer interacting with a fractal surface is dominated by the intersection probability between the polymer and the fractal surface and not so much the particular "shape" of the surface. Obviously comparison between such an idealized model and Monte Carlo data is required before the model can be taken too seriously.

Comparison of the ES model with Monte Carlo data by Stella[10] for the partition function of a polymer interacting (absorbing boundary conditions) with a fractal surface (a triadic Koch curve; see Mandelbrot[4] and Kohring[11] for illustration) in two dimensions yields good agreement. This is encouraging since the ES model also compared well in its previous application to a Gaussian polymer interacting with random impurities[9] and to the dimensions of a block within a diblock copolymer.[12] A comparison of the ES model is also made with Monte Carlo data for polymer collapse with encouraging results. In this instance the polymer is its own effective surface and "collapse" corresponds to "self-adsorption".

Section 2 introduces the ES model and establishes notational conventions. In section 3 the model is tested against Monte Carlo data for the partition function of a polymer at a fractal boundary. Some exact results for a polymer in a wedge are summarized, since this type of boundary is sometimes used as a rough model of a fractal boundary. The effect of excluded volume on the mean dimensions of an interacting polymer at a plane boundary is discussed by using the ES model and the results are compared with Monte Carlo simulation data and renormalization group calculations.

Section 4 considers adsorption of polymers at fractal surfaces and universal expressions for the free energy and correlation length describing the adsorbed polymer are derived as functions of the chain and surface fractal dimensions. The effect of roughness on the critical adsorption temperature, the adsorption Θ point,[1] is qualitatively estimated. The ES model is used to calculate the free energy of a collapsing polymer and the result is compared with recent Monte Carlo data. More technical aspects of the discussion are given in appendices.

2. The "Effective Surface" Model

Recent calculations by Kosmas[13] and Douglas et al.[14] consider the problem of a surface interacting polymer where the surface dimension is variable. The early calculations by Kosmas[13] involve the renormalization group ϵ-perturbation theory, while the calculations of Douglas et al.[14] solve exactly the model of a Gaussian chain interacting with the variable-dimension surface. Calculations by Kosmas[13] and Douglas et al.[14] incorporate excluded-volume interactions into the model using the renormalization group theory. To fix notation we briefly introduce the model of a polymer interacting with a variable-dimension surface and review some results relevant to our purposes here.

The polymer is modeled by a continuous Gaussian chain specified by a position vector $\mathbf{R}(x)$ at a contour distance x along a chain of unit length N. The chain is composed of n Kuhn links of length l, $N = nl$, and has a mean-square end-to-end distance of $\langle \mathbf{R}^2 \rangle_{0f} = nl^2$ in the absence of interactions (a "free" chain). In the units of $K_B T$, the unperturbed Hamiltonian is

$$\mathcal{H}_0 = (1/2) \int_0^1 \mathrm{d}x \, |\mathrm{d}\mathbf{r}(x)/\mathrm{d}x|^2; \qquad \mathbf{r}(x) = (d/\langle \mathbf{R}^2 \rangle_{0f})^{1/2} \mathbf{R}(x) \quad (2.1)$$

Next we add a pseudopotential (δ-function) surface interaction in dimensionless units[13,14]

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

$$z_s^{\,0} = (d/2\pi l^2)^{d_\perp/2} \beta_s^{\,0} n^{\phi_s}, \qquad \phi_s = \epsilon_\perp/2 \quad (2.3)$$

$$\epsilon_\perp = 2 - d_\perp = (2 + d_\parallel) - d, \qquad d_\perp + d_\parallel = d \quad (2.4)$$

where the surface is a Euclidean hypersurface of dimension $d_\parallel$ embedded in a space of dimension d, $\beta_s^{\,0}$ is a surface interaction coupling constant, and ϕ_s is the crossover exponent for a Gaussian chain interacting with a surface. The position vectors $\mathbf{R}_\perp$ and $\mathbf{R}_\parallel$ and their dimensionless counterparts

$$\mathbf{r}_\parallel(x) = (d/\langle \mathbf{R}^2 \rangle_{0f})^{1/2} \mathbf{R}_\parallel(x); \qquad \mathbf{r}_\perp(x) = (d/\langle \mathbf{R}^2 \rangle_{0f})^{1/2} \mathbf{R}_\perp(x) \quad (2.5)$$

are the projections of $\mathbf{R}$ onto the $d_\parallel$-dimension surface and the "orthogonal" space of dimension $d_\perp$. For concreteness the surface dimensions $d_\parallel = 0$, $d_\parallel = 1$, ... correspond to a point, line, etc. and having variable $d_\parallel$ provides a means for describing the effect of surface dimension in a unified way. The variability of $d_\parallel$ is exploited in the effective surface model introduced below.

There are also polymer–polymer excluded-volume interactions that should be considered. Here attention is confined to binary excluded-volume interactions[15] (the two-parameter model):

$$\mathcal{H}_2(\text{polymer–polymer}) = (z_2^{\,0}/2!) \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}x' \, \delta[\mathbf{r}(x) - \mathbf{r}(x')] (2\pi)^{d/2} \quad (2.6)$$

$$z_2^{\,0} = (d/2\pi l^2)^{d/2} \beta_2^{\,0} n^{\phi_2}, \qquad \phi_2 = \epsilon/2, \quad \epsilon = 4 - d \quad (2.7)$$

It is evident from previous calculations that the most important parameters characterizing the effect of dimension on surface interacting polymers with excluded volume are the crossover exponents (ϕ_s, ϕ_2). The ϵ-expansion method of the renormalization group theory is an expansion about the limit where the crossover exponent is small and perturbation theory is meaningful (i.e., $z_s^{\,0}$ and $z_2^{\,0}$ are not too large). Beyond providing a measure of polymer interactions as a function of dimension, the crossover exponent has a direct geometric significance, which is used in motivating the effective surface model.

The crossover exponent ϕ_s provides a measure of the probability that the random walk encounters a surface. Strong mathematical arguments (rigorous in $d = 1$) indicate that the fractal (Hausdorff) dimension of the set of contour points for a simple random walk striking a fractal surface of dimension d_{fs} embedded in d-dimensional space is given by[16,17]

$$(2 + d_{fs} - d)/2 \quad (2.8a)$$

For a Euclidean surface we have $d_{fs} = d_\parallel$ and (2.8a) reduces to the definition of ϕ_s in (2.3). The crossover exponent then defines the fractal dimension of the contour points along the chain (the "occupation time") which strike a penetrable surface of dimension $d_\parallel$. More generally for Lêvy flight type random walks (see Appendix A) in which the fractal dimension of the chain is variable (mimicking in many respects the physically more interesting self-avoiding chains; see below) we have for the occupation time fractal dimension[16,17]

$$(d_{fc} + d_{fs} - d)/d_{fc} \quad (2.8b)$$

Equation 2.8 equals the crossover exponent for a surface-interacting Lêvy flight (see Appendix A) and the special case of $d_{fc} = 2$ corresponds to simple random walks and (2.8a). It is perhaps worth reviewing the physical significance of d_{fc}.

The fractal dimension of the chain d_{fc} simply characterizes the distribution of chain mass in space and is directly related to the molecular weight dependence of the chain radius R as measured, for example, by the polymer radius of gyration. If the chain radius scales with molecular weight according to the power law

$$R \sim M^\nu \quad (2.9a)$$

then the fractal dimension[4] of chain is defined as

$$d_{fc} = 1/\nu, \qquad d > d_{fc} \quad (2.9b)$$

For a Gaussian chain we have the familiar result, $R \sim M^{1/2}$, so that $d_{fc} = 2$, while a swollen chain has a fractal dimension

$$R(\text{swollen}) \sim M^\nu; \qquad \nu \approx 3/(d + 2);$$
$$d_{fc} \approx (d + 2)/3; \qquad 2 < d < 4$$

if the Flory estimate of ν is used (see ref 15). For a rigorous discussion of the fractal dimension d_{fc}, see Taylor.[18]

The fundamental ansatz leading to the "effective surface" model is that the crossover exponent ϕ_s for fractal surface [see (2.8)] interacting polymers equals

$$\phi_s \leftrightarrow \hat{\phi}_s = (d_{fc} + d_{fs} - d)/d_{fc} \quad (2.10)$$

where the circumflex reminds us that we are only considering a geometrically motivated model of the fractal surface and the variable fractal dimension of the polymer chain. In other words we "identify" $d_\parallel$ with d_{fc} on the basis of the geometric arguments above. It is emphatically not an exact description in all instances but captures many of the salient features of problems that can only be approached at the present time by involved renormalization group calculations or Monte Carlo simulation. We now proceed to a comparison of the model with available simulation data and analytic calculations.

3. Tests of the Effective Surface Model: Absorbing Boundary Conditions

Stella[10] has recently performed Monte Carlo simulations for random walks interacting with fractals having variable surface dimension in two dimensions and his results provide a test of the effective surface model. Stella finds that the number of configurations Q of a chain (no excluded volume) terminally attached to a fractal curve of dimension d_{fs} scales as (see ref 20)

$$Q \sim Q_0 n^{\gamma_s - 1}, \qquad d = 2 \tag{3.1a}$$

$$\gamma_s - 1 \approx -d_{\mathrm{fs}}/2 \tag{3.1b}$$

The boundary condition on the fractal is absorbing and the results are independent of the side of the surface on which the chain is terminally attached.[20] Equation 3.1 holds for various fractals, such as the classical Koch curve where the fractal dimension is variable.[4] Q_0 denotes the partition function Q for a chain in the absence of a surface.

Exact calculations for a terminally attached chain interacting with a variable-dimension surface give[14]

$$Q \sim Q_0 n^{\gamma_s - 1}, \qquad \gamma_s - 1 = -\phi_s, \qquad 0 < \phi_s < 1 \tag{3.2a}$$

The effective surface analogy implies $\phi_s \to \hat{\phi}_s$ given in (2.10) and predicts

$$\gamma_s - 1 = -\hat{\phi}_s = -[2 + d_{\mathrm{fs}} - d]/2 \tag{3.2b}$$

Inserting $d = 2$ in (3.2b) exactly recovers (3.1b). Predictions for other exponents are given in ref 14, but the Monte Carlo data are unavailable.

The qualitative trend in the properties of a polymer at a surface can be understood from the exactly solvable models of a polymer confined in a wedge or in a cone. These results are worth mentioning since they are not well-known and because they potentially provide a starting point for rigorous analytic calculations of polymers at fractal surfaces.

The γ exponents for a polymer attached to the apex of an absorbing boundary wedge of angle α are obtained by replacing ϕ_s in (3.2) by $(\pi/2\alpha)$. This result was first obtained by Lauritzen and Di Marzio[21] and can be readily understood as a consequence of a standard conformal mapping ($w = z^{\pi/\alpha}$) of the wedge geometry into a half-plane.[22] Crudely, the fractal surface can be modeled by a wedge with an angle chosen to mimic the more complicated fractal structure. Such a procedure has been frequently employed in modeling the growing surface of diffusion-limited aggregates where the ratio $\pi/2\alpha$ is heuristically related to the fractal dimension of the aggregate.[23] Cardy generalized the wedge calculations to self-avoiding chains and recently reviewed numerous calculations relating to this problem.[24] An exact treatment of a polymer at a Koch-type fractal[11] boundary in $d = 2$ dimensions should be possible employing an iterated conformal mapping of the boundary paralleling Mandelbrot's "generator" construction of the Koch curve.[4] The Schwartz-Christoffel[22] method could be employed to map the crumpled boundary back into a more tractable boundary.

A test of treating the chain fractal dimension as variable in the effective surface model can be made by recalling first-order renormalization group results for self-avoiding chains at an absorbing boundary. For example, the mean-square end-to-end distance $\langle \mathbf{R}^2 \rangle$ for a Gaussian chain terminally attached to an absorbing (i.e., "repulsive") boundary of variable dimension equals[14]

$$\gamma_{R^2} = \langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_{0\mathrm{f}} = 1 + (d_\perp/d)\phi_s/(1 - \phi_s), \qquad 0 < \phi_s < 1 \tag{3.3a}$$

The zero subscript on $\langle \mathbf{R}^2 \rangle_{0\mathrm{f}}$ denotes the mean dimensions of a chain in the absence of a surface. A special and well-known case of $\gamma_R{}^2$ corresponds to an absorbing two-dimensional surface in three dimensions where $\gamma_R{}^2 = {}^4/_3$, a result first derived by Rubin.[25]

For a chain with excluded volume in three dimensions, we may approximate ν by the Flory value $\nu(d{=}3) = {}^3/_5$ and consider a two-dimensional surface to obtain the effective surface model estimate

$$\gamma_{R^2} = \langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_{\mathrm{f}} = 11/9 \approx 1.22 \tag{3.3b}$$

where the free-chain dimensions correspond to a chain with excluded volume. Renormalization group calculations for a terminally attached chain with excluded volume at an absorbing boundary give[14]

$$\gamma_{R^2}(\mathrm{SAW}; d{=}3; d_\parallel{=}2) \approx 1.18 \tag{3.3c}$$

$$\gamma_{R^2}(\mathrm{SAW}; d{=}3; d_\parallel{=}2) \approx 1.20 \tag{3.3d}$$

The two different estimates (3.3c) and (3.3d) correspond to two different perturbative schemes. In (3.3c) the surface dimension is fixed as $d_\parallel = d - 1$, while in the second instance the surface dimension is treated as variable (see ref 1 and 14 for a discussion). Monte Carlo data for γ_{R^2} for a terminally attached chain at a two-dimensional surface with excluded volume indicates[1,26]

$$\gamma_{R^2} \approx 1.2 \tag{3.3e}$$

The effective surface model seems to be quite consistent with previous first order in ϵ RG calculations and the Monte Carlo simulation data.

In future work the author plans to show how the maneuver of formally treating d_{fc} as variable in the ES model provides a unified approximate model of the polymer hydrodynamics, surface interaction, and excluded-volume interaction in fractals.[27] Since this entails a necessarily long digression, we next consider the predictions of the effective surface model for polymer adsorption at rough surfaces.

4. Polymer Adsorption at a Rough Surface

Surface topography can play an important role in understanding polymer adsorption.[2] We all know from everyday experience that roughening a surface tends to improve adhesion. The usual undergraduate level physical chemistry folklore for this effect is that the "surface area" is somehow being increased. "Roughening", of course, involves a number of effects, such as cleaning off the surface layer and modifying the surface chemistry, but it is useful to focus on the purely geometrical consequences of wrecking the surface through some mechanical process. It should be admitted that the extent to which macroscopic roughening propagates to microscopic scales, creating surfaces reasonably approximated by fractals, is not really clear. Pfeifer et al. indicate specific examples of fractals generated by crushing and grinding, which are certainly related processes. It is presumed in the discussion below that roughening "fractalizes" the surface.

The effective surface model provides a framework for describing the more quantitative effects of surface roughness on polymer adsorption. For example, the free energy per monomer unit for a Gaussian chain adsorbed on a variable-dimension surface is equal[14]

$$-\Delta F/nK_BT = \lim_{n \to \infty} [\ln (Q/Q_0)/n] \sim |\beta_s{}^0|^{1/\phi_s}, \qquad 0 < \phi_s < 1 \tag{4.1}$$

At a temperature T near the "adsorption Θ point", Θ_A, where $\beta_s{}^0$ vanishes, we have[1,14]

$$\beta_s{}^0 \sim (T - \Theta_A)/T \tag{4.2}$$

Moreover, the surface correlation length ξ_s describing the "thickness" of the adsorbed polymer equals[14]

$$\xi_s{}^2 \sim |\beta_s{}^0|^{-1/\phi_s} \sim |(T - \Theta_A)/T|^{-1/\phi_s} \tag{4.3}$$

Exact expressions including the numerical prefactors are included in the work of Douglas et al.[14] Replacing ϕ_s by

$\hat{\phi}_s$ in the effective surface model (see Appendix B for a more technical justification) indicates precise predictions for the modification of polymer adsorption by surface roughness and excluded-volume interactions. Replacing ϕ_s in the exact results (4.1) and (4.3) by $\hat{\phi}_s$ in (2.10) implies the free-energy per monomer unit scales as

$$\Delta F/nK_BT \sim |(T-\Theta_A)/T|^{1/\hat{\phi}_s}, \qquad T \le \Theta_A \quad (4.4a)$$

$$1/\hat{\phi}_s = d_{fc}/(d_{fc}+d_{fs}-d) \quad (4.4b)$$

and the surface correlation length then becomes

$$\xi_s^{d_{fc}} \sim |(T-\Theta_A)/T|^{-1/\hat{\phi}_s}, \qquad T \le \Theta \quad (4.5)$$

In three dimensions an increase in d_{fs} decreases $1/\hat{\phi}_s$ relative to $1/\phi_s$ ($d_\parallel = 2$) and thus *sharpens* the phase transition of the polymer onto the surface.[14] Roughening (increase of d_{fs}) leads to a "tighter" adsorption onto the surface (i.e., decreased ξ_s relative to the ideal planar surface). The enhanced adsorption onto the surface arises in the ES model from the enhanced probability of intersecting with the "rough" fractal surface and not so much the increased absolute area of the roughened surface.

Equations 4.4 and 4.5 are also useful for understanding some qualitative nonequilibrium aspects of polymer adsorption. For a strongly attractive plane surface ($d_\parallel = 2$), we can expect portions of a polymer chain to deposit rapidly onto a surface thereby "modifying" the surface on which the remaining part of the chain adsorbs. Such a modified "stringy" surface is akin to a surface decimated by many holes and the effective dimension of the surface can be expected to be *lower* than that of the starting planar surface. Putting a lower value of d_{fs} in (4.5) implies a more diffuse interface for the initial nonequilibrium adsorption, which should gradually "relax" to a more strongly adsorbed configuration through thermal fluctuations.[28] The "sequential adsorption" picture of a strongly adsorbing surface has been discussed previously by Barford et al.[29] using a mean-field model, but the qualitative conclusion is quite similar to the "geometric" interpretation sketched above.

An important factor neglected in the above discussion of adsorption onto fractal surfaces is an accounting of surface roughness on the adsorption Θ temperature Θ_A below which the polymer adsorbs onto the surface. Adsorption at a surface involves a competition between the gain of internal energy in forming attractive surface contacts and the loss of configurational entropy arising from being confined at a surface.[1,26] Since roughening a surface should generally change the local degrees of freedom on the surface, we can anticipate qualitative changes in the adsorption temperature.

A useful estimate of the shift of the adsorption point can be made from exact lattice calculations for adsorption onto Euclidean surfaces of varying dimension and coordination number. Rubin starts with a lattice model with a surface defined to have adsorbing boundary conditions and adds a nearest-neighbor attractive surface interaction (see ref 1). Polymer adsorption occurs when the enthalpic contribution of attractive polymer–surface contacts overcomes the loss of configurational entropy arising from confinement to the surface. In mathematical terms a critical polymer–surface interaction φ_c is defined by

$$\exp(\varphi_c) = q(\text{free})/q(\text{confined}) \quad (4.6)$$

where q is the coordination number of the free chain in the absence of a surface and q(confined) is the effective coordination number of a confined chain. Rubin's exact calculation[25] for $d = 3$ with a lattice of coordination number q_3 and a surface of coordination number q_2 gives q(confined) as the average $q(\text{confined}) = (q_2 + q_3)/2$. Douglas et al.[1] propose an approximate expression for φ_c on hypercubic lattices of dimension d and surface dimension $d_\parallel$

$$\exp(\varphi_c) \approx 2d/(d + d_\parallel) \quad (4.7)$$

If we now treat the surface dimension $d_\parallel$ as being variable in (4.7), formally equating $d_\parallel$ with the surface fractal dimension,[30] we find that an increase of roughness (i.e., d_{fs}) decreases φ_c. This is just a statement that a chain has to lose less configurational entropy to adsorb onto a rough surface. The important implication is that the adsorption temperature Θ_A is raised[31] relative to a flat surface. Thus, by roughening a surface, it may be possible to convert a repulsive interface into an adsorbing interface without modifying the chemical makeup of the surface! It would be very interesting to test (4.7) with $d \approx d_{fs}$ through Monte Carlo simulations of adsorption onto fractals. (4.7) is not expected to be exact but should reproduce the correct qualitative trends.[32] A remarkably accurate generalization of (4.6) to include the effect of excluded volume on φ_c is described by Douglas et al.[1]

It should be noted that the above discussion for the adsorption onto a fractal assumes the fractal has infinite extent. Obviously if the dimensions of the surface are small relative to the dimensions of the polymer then the "effective dimension" of the surface becomes diminished. If the polymer is very much larger than the fractal surface, then the fractal can be modeled as a point corresponding to $d_\parallel = 0$ in the surface interaction model. The increasing surface curvature arising from shrinking the interacting surface should lead to a diminished polymer surface interaction—an effect opposite to increasing the roughness of a fractal surface of infinite extent.

As a final application of the effective surface model we consider the problem of polymer collapse from attractive polymer–polymer interactions. The self-interaction of a polymer [see (2.6) and (2.7)] can be viewed as a *polymer interacting with a surface where the polymer is its own surface*. In this picture the self-avoiding limit corresponds to an adsorbing boundary condition and the Θ point to an effective reflecting boundary condition, while collapse corresponds to self-adsorption. To follow this analogy further we observe that the fractal dimension of the chain and the surface are equal, $d_{fs} = d_{fc} = 2$, so that $\hat{\phi}_s$ in (2.10) becomes

$$\hat{\phi}_s(d_{fc}=d_{fs}=2) = \epsilon/2; \qquad \epsilon = 4 - d \quad (4.8)$$

This is equal to ϕ_2 in (2.7) and the same argument leads to the correct result for the excluded-volume exponent ϕ_2 for Lēvy flights given in Appendix A.

Equation 4.8 of the effective surface model indicates that the free energy of a collapsing polymer equals

$$\Delta F/nK_BT \sim |(T-\Theta)/T|^{2/\epsilon}, \qquad T \le \Theta \quad (4.9a)$$

which is in contrast to the dimensionally independent mean-field result[33]

$$\Delta F/nK_BT \sim |(T-\Theta)/T|^{2}, \qquad T \le \Theta \quad (4.9b)$$

Recently, Ishinabe investigated the temperature dependence of ΔF for self-avoiding chains with an attractive polymer–polymer nearest-neighbor interaction in two and three dimensions.[34] Ishinabe's results are consistent with (4.9a) rather than the mean-field result (4.9b).

A discussion of the collapse of a polymer in a field of dense weakly interacting impurities is given in ref 9, which parallels the treatment here of collapse from self-polymer–polymer attractions. By modeling the random impurities by a fractal dust of dimension d_{fs}, Douglas[9] finds the free energy and confinement length ξ are equal [see (4.4) and (4.9a)] to

$$\Delta F/nK_BT \sim |\beta_I{}^0|^{2/\epsilon} \tag{4.10a}$$

$$\xi^2 \sim |\beta_I{}^0|^{-2/\epsilon} \tag{4.10b}$$

where $\beta_I{}^0$ is a parameter characterizing the impurity density and interaction. $\beta_I{}^0$ vanishes in the limit of no impurities, corresponding to a transition from a collapsed to extended configuration. (4.10a) and (4.10b) have also been obtained recently by Edwards and Muthukumar[8] using replica and variational methods and (4.10b) has been verified in simulation data by Baumgärtner and Muthukumar[6] for $d = 3$.

5. Conclusion

There are many physical situations where an interface is "diffuse" and the idealized geometries of surface-interacting polymers are inadequate. For example, the adsorbent could be a stringy colloidal aggregate, the porous adsorbent in a chromatographic column, or an interface formed by a more or less random deposition of some diffusing substance. There could be small dispersed impurities in solution or we might even consider adsorption of one polymer onto another polymer. Diffuse adsorbents are no doubt commonly encountered in nature and are perhaps more of a rule than an exception.

Because of the difficulty of incorporating boundary conditions for fractal surfaces into the diffusion equation (or equivalent path integral) describing the polymer configurations, most studies employ a combination of model building, scaling, and simulation methods. The model of treating a fractal surface as an "effective surface" (ES) of fractional dimension provides numerous quantitative predictions for polymer properties at a diffuse interface. According to the ES model, increasing the fractal dimension of the surface will sharpen the phase transition (see Appendix A of ref 14a) of surface adsorption, since the free energy per monomer unit of an adsorbed Gaussian chain scales as

$$\Delta F/nK_BT \sim (T - \Theta_A)^{2/(2+d_{fs}-d)}$$

where d_{fs} is the fractal dimension of the surface ($d_{fs} = 2$ if the Gaussian chain is interacting with itself) and Θ_A is the adsorption Θ point where the surface interaction coupling constant vanishes. According to the same reasoning, the surface correlation length, describing the "thickness" of the adsorbed layer, becomes smaller with increased fractal dimension, leading to tighter binding with increasing roughness as measured by d_{fs}. The opposite trend is predicted if the surface is "decimated" by many holes so as to reduce its fractal dimension. This later situation is relevant, for example, in understanding nonequilibrium aspects of "strong" adsorption.

Finally, the effective surface analogy is used to argue that polymer adsorption should occur more readily on fractal surfaces, since there is less of an entropic cost in such adsorption. Exact results for adsorption on lattice Euclidean surfaces are used to estimate this effect qualitatively.

The ES model is tested against recent Monte Carlo data for random walks interacting with fractal surfaces and previous comparisons of the model are recalled. These comparisons lead to encouraging results.

A more general model to test the effective surface analogy further is to consider a block copolymer where one "block" is a tethered surface[35] (a natural generalization of the Hamiltonian (2.1) to a polymer of sheetlike connectivity) and the other block is a conventional linear polymer. The arguments given in this paper suggest that the crumpling and swelling of the "sheetlike" polymer could induce an adsorption–desorption transition in the attached linear polymer. It would be interesting to explore this effect in Monte Carlo simulations. There is also the interesting possibility that the fractal dimension of random surfaces (such as organelles in cells[3]) could selectively adsorb polymers by "tuning" their surface fractal dimension. Lewis and Rees[3b] have recently noted that regions on a protein surface involved in forming strong complexes appear rougher than regions forming transient complexes.

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Appendix A. Lèvy Flight Interacting with a Point

The Gaussian chain model (2.1) corresponds to a universal continuum limit of a whole class of discrete random walk models in which the mean-square step length $\langle \mathbf{l}^2 \rangle$ is constrained to be finite. The characteristic feature of this kind of random walk is that the mean-square end-to-end distance $\langle \mathbf{R}^2 \rangle$ of the chain as a whole is asymptotically (limit of larger number of steps n) proportional to $\langle \mathbf{R}^2 \rangle_0 \propto n\langle \mathbf{l}^2 \rangle$ due to the independence of the chain steps.

A more general type of random walk is obtained by introducing a less restrictive "norm" (measure of size) on the step length $\mathbf{l}$. The weaker constraint that $\langle |\mathbf{l}|^{d_{fc}} \rangle$ is finite (d_{fc} is the fractal dimension of the random walk) leads to the Lèvy flight type random walks, which specialize to the "simple" random flight type walks mentioned above when $d_{fc} \to 2$. Because each step of the random flight is independent, the dimensions (a generalized moment[36]) of the entire chain are again proportional to n times the average size of each step $\langle |\mathbf{R}|^{d_{fc}} \rangle_0 \propto n\langle |\mathbf{l}|^{d_{fc}} \rangle$, giving the appropriate average measure of size for this type of walk. The average radius R_0 then scales as

$$R_0 \equiv \langle |\mathbf{R}|^{d_{fc}} \rangle_0{}^{1/d_{fc}} \sim n^{1/d_{fc}} \sim n^{\nu}; \qquad \nu \equiv 1/d_{fc} \tag{A.1}$$

where the reciprocal of the chain's "fractal dimension" is denoted[37] by ν. There are some mathematical complications brought about by the fact that the moment $\langle |\mathbf{R}|^{\alpha} \rangle_0$ diverges for $\alpha > d_{fc}$ (see ref 31 and 32) when $\alpha \neq 2$. Decreasing d_{fc} has the obvious consequence of allowing for random walk jumps of greater length, giving rise to chains that extend on average to greater distances in space relative to their Gaussian counterparts ($d_{fc} = 2$). Qualitatively, this situation is similar to the addition of excluded volume to the Gaussian chain model where the exponent ν likewise increases.

Some insight into the problem of a surface interacting chain with excluded volume can be obtained by considering a surface-interacting Lèvy flight. This approach exhibits the qualitative effect of varying the exponent ν, as mentioned above, and has the advantage that exact calculations are possible. The model also provides an example for which the ES model is *exact*.

First, a dimensional analysis indicates the qualitative effect of varying the exponent ν. Although the unperturbed Hamiltonian $\mathcal{H}_0$(Lèvy) requires generalization from the Wiener form (2.1) (see Prentis[38]), the interactions remain the same as in (2.2) and (2.6) and the diagrammatic expansion of the perturbation theory is also unchanged. Introducing the reduced units of distance appropriate to the Lèvy flight model gives

$$\hat{\mathbf{r}}_\perp = \mathbf{R}_\perp/R_0; \qquad \hat{\mathbf{r}} = \mathbf{R}/R_0 \tag{A.2}$$

The interaction Hamiltonians (2.2) and (2.6) are then rewritten using (B.2) to obtain the dimensionless representation

$$\mathcal{H}_s(\text{Lèvy}) = \hat{\beta}_s{}^0 \int_0^1 \mathrm{d}x\ \delta[\hat{\mathbf{r}}_\perp(x)] \tag{A.3a}$$

$$\mathcal{H}_2(\text{Lèvy}) = \hat{z}_2{}^0 \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}x'\, \delta[\hat{\mathbf{r}}(x) - \hat{\mathbf{r}}(x')] \tag{A.3b}$$

where the dimensionless interaction parameters are defined as[14]

$$\hat{z}_s{}^0 \propto \beta_s{}^0 n^{\phi_{\mathrm{SL}}}; \qquad \phi_{\mathrm{SL}} = (1/\nu + d_\parallel - d)\nu \tag{A.4a}$$

$$\hat{z}_2{}^0 \propto \beta_2{}^0 n^{\phi_{2\mathrm{L}}}; \qquad \phi_{2\mathrm{L}} = (2/\nu - d)\nu \tag{A.4b}$$

Note that the critical dimensions of the surface *and* excluded-volume interactions (corresponding to the vanishing of ϕ_{SL} are $\phi_{2\mathrm{L}}$) are in general functions of the fractal dimension ($d_{\mathrm{fc}} = 1/\nu$) of the chain. Compare (A.4a) with (2.10). The ϵ-parameters of the surface and excluded-volume perturbation theories are defined through (A.4) as

$$\phi_{\mathrm{SL}} = \hat{\epsilon}_\perp \nu; \qquad \hat{\epsilon}_\perp = 1/\nu + d_\parallel - d = d_{\mathrm{fc}} + d_\parallel - d \tag{A.5a}$$

$$\phi_{2\mathrm{L}} = \hat{\epsilon}_2 \nu; \qquad \hat{\epsilon}_2 = 2/\nu - d = 2d_{\mathrm{fc}} - d \tag{A.5b}$$

and reduce to (2.3) and (2.7) for the special case of $d_{\mathrm{fc}} = 2$.

Prentis[38] discusses the perturbation expansion of Lêvy flights ("node avoiding") with excluded volume, which is a generalization of the standard two-parameter model. He calculates the modification of the exponent ν due to excluded volume by applying RG arguments to the Lêvy flight two-parameter perturbation series. Corrections are obtained in a series in $\hat{\epsilon}_2$ [see (A.5b)], which reduce to the standard RG predictions for simple self-avoiding walks when $d_{\mathrm{fc}} = 2$ ($\nu = {}^1/_2$).

The perturbation expansion for a surface-interacting Lêvy flight extends the work of Kosmas[13] and Douglas et al.[14] for surface-interacting Gaussian chains and the work of Prentis[38] on self-avoiding Lêvy flights. To illustrate the method consider the Fourier–Laplace transform of the Lêvy flight end-vector distribution function (see Prentis[38] for details where his μ is equal d_{fc} above)

$$G_0(q,s) = 1/(q^{d_{\mathrm{fc}}} + s) \tag{A.6}$$

where $q = |\mathbf{q}|$ is Fourier variable conjugate to the position vector $\mathbf{R}$ and s is the Laplace transform variable conjugate to the chain length n. Further, the surface dimension is *restricted to zero*, $d_\parallel = 0$, corresponding to the Lêvy flight interacting with its end point. The more general case of $d_\parallel \neq 0$ leads to more complicated algebra but the $d_\parallel = 0$ case serves to illustrate the general ideas.

The perturbation expansion is the same as described by Douglas et al.[7] for surface-interacting chains, except that now the calculations are performed in the conjugate Fourier–Laplace transform notation. For example, the end-vector distribution for Lêvy flights interacting with their end point (situated at the origin) has the form

$$G(q,s) = G_0(q,s)\left[1 + \hat{\beta}_s{}^0 \int \mathrm{d}^d\mathbf{q}/(q^{d_{\mathrm{fc}}} + s)\right]^{-1} \tag{A.7}$$

where uninteresting geometrical constants are absorbed into the surface interaction coupling parameter $\hat{\beta}_s{}^0$. This form of $G(q,s)$ also corresponds for $d_{\mathrm{fc}} = 2$ to a specialization of $G(q,s)$ for the $O(n)$ field theory model with a point defect (see Wang and Freed[39]), and because of this redundancy we are brief.

The integral in (A.7) is trivial and an exact expression for the interacting Lêvy flight partition function is easily obtained. Performing the integral in (A.7) gives

$$G(q,s) = G_0(q,s)[1 + \hat{\beta}_s{}^0 \Gamma(\hat{\epsilon}_\perp \nu) s^{-\phi_{\mathrm{SL}}}]^{-1} \tag{A.8}$$

where some uninteresting geometric constants are again absorbed into $\beta_s{}^0$. The "susceptibility" is obtained from the $q \to 0$ limit of $G(q,s)$ as

$$\chi(s) = G(q \to 0,s) = s^{-1}[1 + \hat{\beta}_s{}^0 \Gamma(\hat{\epsilon}_\perp \nu) s^{-\phi_{\mathrm{SL}}}]^{-1} \tag{A.9}$$

and is equal to the Laplace transform of the partition function of the interacting Lêvy flight. Furthermore, long chains correspond to the $s \to 0$ limit where we have

$$\lim_{s \to 0} \chi(s) \sim s^{-1+\phi_{\mathrm{SL}}} \tag{A.10}$$

so that upon Laplace inversion the partition function Q has the asymptotic behavior ($\hat{z}_s{}^0 \to \infty$)

$$Q(\hat{z}_s{}^0) \sim n^{\gamma_s - 1}; \qquad \gamma_s - 1 = -\phi_{\mathrm{SL}} \tag{A.11}$$

The same result may be obtained by applying RG arguments to the perturbation expansion.[14] The full inversion of the Laplace transform (A.9) can easily be made by noting that the inversion

$$\mathcal{L}_s{}^{-1}\{\chi(s,d_{\mathrm{fc}}{=}2)\} = \mathcal{L}_s{}^{-1}\{s^{-1}[1 + \hat{\beta}_s{}^0 \Gamma(\epsilon_\perp/2) s^{-\epsilon_\perp/2}]^{-1}\} \qquad \epsilon_\perp \in (0,2) \tag{A.12}$$

for Gaussian chains is the *same* as for (A.8) except ϕ_{SL} is simply *replaced* by $\phi_s = \epsilon_\perp/2$. The partition function $Q = \mathcal{L}^{-1}\{\chi(s)\}$ for Gaussian chains is the Mittag-Leffler function of index $\epsilon_\perp/2$, so that we obtain in general for a point-interacting Lêvy flight

$$Q(\text{Lêvy}) = \sum_{k=0}^{\infty} [-\hat{z}_s{}^0 \Gamma(\phi_{\mathrm{SL}})]^k / \Gamma(1 + k\phi_{\mathrm{SL}}); \qquad \phi_{\mathrm{SL}} \in (0,1) \tag{A.13}$$

which is the Mittag-Leffler function of index ϕ_{SL}. The effective surface analogy defined by (2.10) with $d_{\mathrm{fs}} = 0$ is *exact* when $\phi_s = \epsilon_\perp/2$ is replaced by its Lêvy flight counterpart ϕ_{SL} ($d_\parallel = 0$). This result is not surprising given the invariance principle discussed in ref 14b, which generalizes the discussion in Appendix B. The Mittag-Leffler function arises frequently in the study of Lêvy flights and related random walk problems (see Chung and Kac and Bingham[40]).

Appendix B. Invariance Principle for the Polymer Free Energy

The ES model is particularly effective in treating problems involving localization of a polymer (adsorption, collapse, etc.) and is especially useful given the failure of the renormalization group theory to describe this kind of phenomena.[14] The success of the method can be understood from a general mathematical principle that is really the "substance" behind the formal ES model.

Kac[41] showed that if we consider a rather arbitrary interaction Hamiltonian given by

$$\mathcal{H}_{\mathrm{I}} = \int_0^n V[\mathbf{R}(\tau)]\, \mathrm{d}\tau, \qquad l = 1, \quad N = n \tag{B.1}$$

where the potential $V[\mathbf{R}(\tau)]$ is chosen such that a bound (i.e., "localized") state exists and such that the unperturbed Hamiltonian is given by (2.1), then the partition function Q of such an interacting chain has a universal limit

$$\lim_{n \to \infty} [\ln (Q/Q_0)/n] \sim E_0, \qquad Q_0 = Q(V{=}0) \tag{B.2}$$

The E_0 in (B.2) is the lowest ("ground-state dominant") eigenvalue of the bound-state spectrum. Equation 4.1 is just a special case of Kac's "invariance principle" (B.2). Even if we don't know the particular nature of the potential beyond a qualitative understanding that the chain is localized, we can infer that (B.2) is the inevitable limit for E_0, the free energy per monomer unit of a localized chain. de Gennes gives numerous applications of (B.2) to problems of practical interest.[42]

The nonanalytic dependence of E_0 on the interaction coupling parameters such as in (4.1), (4.4), (4.9), and (4.10) can be understood rather simply as a further consequence of Kac's invariance principle (B.2) with the specialization to homogeneous potentials.

First, we observe that the strength of a perturbing potential $V[\mathbf{R}]$ is generally characterized by a "coupling constant" [e.g., β_s^0 in (2.3)], so without loss of generality we define[14]

$$V_{\mathrm{H}}[\mathbf{R}] = \beta^0{}_{\mathrm{Hom}} v_{\mathrm{H}}[\mathbf{R}] \qquad \text{(B.3a)}$$

where $\beta^0{}_{\mathrm{Hom}}$ is a parameter that absorbs all our energy units. A homogeneous potential has the property

$$V_{\mathrm{H}}(\lambda\mathbf{R}) = \lambda^h V_{\mathrm{H}}(\mathbf{R}) \qquad \text{(B.3b)}$$

such that h and λ are constants. Introducing dimensionless units in (B.1) as

$$\mathbf{R}(\tau) = \mathbf{r}(\tau)/\langle\mathbf{R}^2\rangle_{0\mathrm{f}}{}^{1/2}; \qquad x = \tau/n \qquad \text{(B.4)}$$

yields the dimensionless form of the Hamiltonian

$$\mathcal{H}_{\mathrm{Hom}} = z^0{}_{\mathrm{Hom}} \int_0^1 v_{\mathrm{H}}[\mathbf{r}(x)]\,\mathrm{d}x \qquad \text{(B.5a)}$$

$$z_{\mathrm{Hom}} \propto \beta^0{}_{\mathrm{Hom}} n^{\phi_{\mathrm{Hom}}}; \qquad \phi_{\mathrm{Hom}} = (2 + h)/2 \qquad \text{(B.5b)}$$

For Lèvy flight type random walks (see Appendix A) the generalization for ϕ_{Hom} is obviously

$$\hat{\phi}_{\mathrm{Hom}}(\text{Lévy}) = (d_{\mathrm{fc}} + h)/d_{\mathrm{fc}} \qquad \text{(B.5c)}$$

Below we specialize to $d_{\mathrm{fc}} = 2$ unless otherwise noted.

Kac's invariance principle implies the partition function for (B.1) with a homogeneous potential scales as

$$\ln\,(Q/Q_0) \sim E_0(\beta^0{}_{\mathrm{Hom}})n; \qquad n \to \infty \qquad \text{(B.6)}$$

with the functional dependence of E_0 on $\beta^0{}_{\mathrm{Hom}}$ unspecified. However, Q/Q_0 must be a function of the dimensionless interaction $z^0{}_{\mathrm{Hom}}$ so that we must have scaling consistency between the equations

$$E_0(\beta^0{}_{\mathrm{Hom}})n \sim f(z^0{}_{\mathrm{Hom}}) \qquad \text{(B.7)}$$

where $f(z^0{}_{\mathrm{Hom}})$ is another unspecified function. Consistency requires

$$E_0(\beta^0{}_{\mathrm{Hom}})n \sim |z^0{}_{\mathrm{Hom}}|^{1/\phi_{\mathrm{Hom}}} \qquad \text{(B.8)}$$

since $(z^0{}_{\mathrm{Hom}})^{1/\phi_{\mathrm{Hom}}}$ is proportional to n. We then obtain a generalization of Kac's invariance principle to homogeneous potentials of order h

$$\lim_{n\to\infty}\left[\frac{1}{n}\ln\,(Q/Q_0)\right] = \frac{\Delta F}{nk_{\mathrm{B}}T} \sim |z^0{}_{\mathrm{Hom}}|^{1/\phi_{\mathrm{Hom}}}/n \sim |\beta^0{}_{\mathrm{Hom}}|^{1/\phi_{\mathrm{Hom}}} \qquad \text{(B.9a)}$$

$$\phi_{\mathrm{Hom}} = (2 + h)/2; \qquad 0 < \phi_{\mathrm{Hom}} < 1 \qquad \text{(B.9b)}$$

Observe that (4.1), (4.4), and (4.9) are just special cases of (B.9). The Kac invariance principle (B.9) controls the phase transition order of polymers in many situations (see ref 14).

Given the invariance principle (B.9) we only need a means of estimating ϕ_{Hom} to characterize the localization transition in complicated situations such as the collapse in the presence of random impurities. In many instances the crossover exponent ϕ_{Hom} simply reflects some geometric property of random walks such as the intersection probability between random walk and some fractal set. Help by mathematicians who specialize on this problem is useful at this point.[18] The effective surface model is useful in instances where ϕ_{Hom} can be estimated from physical considerations and fed into (B.9).

The connection between the energy E_0 and the confinement correlation length ξ in section 5 needs some explanation and again the Kac invariance principle is an indispensible tool. The polymer partition function Q is obtained by integrating the end-to-end distribution function, which is a function of $\beta^0{}_{\mathrm{Hom}}$ and $\mathbf{r}$ [see (B.4)]. Integration over $\mathbf{R}$ implies that Q is a function of $\beta^0{}_{\mathrm{Hom}}$ and $\langle\mathbf{R}^2\rangle_{0\mathrm{f}}$. Obviously for Lèvy flights we need to consider the generalized moments of Appendix A, so we specialize to Gaussian chains. The Kac invariance principle for Gaussian chains is then

$$\ln\,[Q(\beta^0{}_{\mathrm{Hom}};\langle\mathbf{R}^2\rangle_{0\mathrm{f}})/Q_0] \sim n, \qquad n \to \infty \qquad \text{(B.10a)}$$

Further we introduce a length scale ξ defined as an unspecified function of $\beta^0{}_{\mathrm{Hom}}$ to obtain the arguments of the dimensionless function Q/Q_0 in terms of the dimensionless variable $\langle\mathbf{R}^2\rangle_{0\mathrm{f}}/\xi^2$. Equation B.10 then is equal to

$$\ln\,[Q(\langle\mathbf{R}^2\rangle_{0\mathrm{f}}/\xi^2)/Q_0] \sim n; \qquad n \to \infty \qquad \text{(B.10b)}$$

Since $\langle\mathbf{R}^2\rangle_{0\mathrm{f}}$ scales as $\langle\mathbf{R}^2\rangle_{0\mathrm{f}} \sim n$, we have an interesting alternate form of Kac's invariance principle

$$\ln\,(Q/Q_0) \sim \langle\mathbf{R}^2\rangle_{0\mathrm{f}}/\xi^2, \qquad n \to \infty \text{ (Gaussian chains)} \qquad \text{(B.11a)}$$

For the special case of homogeneous potentials, (B.9) and (B.11) imply

$$\xi^2{}_{\mathrm{Hom}} \sim \langle\mathbf{R}^2\rangle_{0\mathrm{f}}|z^0{}_{\mathrm{Hom}}|^{-1/\phi_{\mathrm{Hom}}}, \qquad n \to \infty \text{ (Gaussian chains)} \qquad \text{(B.12)}$$

which is written in terms of the coupling parameter $\beta^0{}_{\mathrm{Hom}}$ as

$$\xi^2{}_{\mathrm{Hom}} \sim |\beta^0{}_{\mathrm{Hom}}|^{-1/\phi_{\mathrm{Hom}}} \qquad \text{(B.13a)}$$

More generally for a random walk in which the average dimensions R_0 scale as $R_0 \sim n^\nu$ (see Appendix A), the same argument for the Gaussian chain case leads to

$$\xi_{\mathrm{Hom}}{}^{d_{\mathrm{fc}}} \sim |\beta^0{}_{\mathrm{Hom}}|^{-1/\hat{\phi}_{\mathrm{Hom}}}, \qquad n \to \infty, \quad R_0 \sim n^\nu \qquad \text{(B.13b)}$$

while (B.11a) becomes

$$\ln\,(Q/Q_0) \sim R_0{}^{d_{\mathrm{fc}}}/\xi_{\mathrm{Hom}}{}^{d_{\mathrm{fc}}}, \qquad n \to \infty \qquad \text{(B.11b)}$$

$$R_0 \sim n^\nu, \qquad d_{\mathrm{fc}} = 1/\nu \qquad \text{(B.11c)}$$

Equations 4.3 and 4.5a are just special cases of (B.11b) and (B.13b). See pages 35, 51, and 251 of de Gennes[42] for applications of (B.11a) and (B.11b). The significance of the ξ_{Hom} parameter is that the end-to-end distribution function is a function of $|\mathbf{R}|/\langle\mathbf{R}^2\rangle^{1/2}$ for a free noninteracting chain, but with localization the mean dimensions refer to the new length ξ_{Hom}, the correlation length, and the end-to-end distribution becomes a function of $|\mathbf{R}|/\xi_{\mathrm{Hom}}$.

In many instances it is useful to have a direct connection between E_0 and the confinement length ξ, which is not restricted to the $n \to \infty$ limit. For strong localization we are led inescapably by Kac's invariance principle [see (B.6) and (B.11B)] to the simple relation

$$\xi_{\mathrm{Hom}} \sim |E_0|^{1/d_{\mathrm{fc}}}, \qquad |z^0{}_{\mathrm{Hom}}| \gg 1 \qquad \text{(B.14a)}$$

and for Gaussian chains ($d_{\mathrm{fc}} = 2$)

$$\xi_{\mathrm{Hom}} \sim |E_0|^{-1/2}, \qquad |z^0{}_{\mathrm{Hom}}| \gg 1 \qquad \text{(B.14b)}$$

Near the transition point $\beta^0{}_{\mathrm{Hom}} \approx 0$ the scaling relation between ξ_{Hom} and E_0 reflects the homogeneity power of the potential. Homogeneous potentials satisfy another basic property relating the energy eigenvalues such as E_0 to expectation values of the interaction Hamiltonian. According to the virial theorem the expectation value of interaction Hamiltonian is given by

$$\langle -\mathcal{H}_{\mathrm{Hom}} \rangle_0 = \left\langle \int_0^n V_{\mathrm{Hom}}[\mathbf{R}(\tau)]\, \mathrm{d}\tau \right\rangle \approx E_0 n / \phi_{\mathrm{Hom}} \qquad \text{(B.15a)}$$

$$\langle -\mathcal{H}_{\mathrm{Hom}} \rangle_0 = \mathrm{d}(\log Q)/\mathrm{d}(\log z^0{}_{\mathrm{Hom}}), \qquad 0 < \phi_{\mathrm{Hom}} < 1 \quad \text{(B.15b)}$$

where the "0" subscript indicates an average corresponding to the lowest energy eigenvalue of the spectrum. The virial theorem relates expectation values of kinetic and potential energies in elementary mechanics (see ref 42) and applies under more restrictive conditions to quantum mechanics and analogue polymer problems. For a very small interaction $|z^0{}_{\mathrm{Hom}}| \ll 1$, we can calculate $\langle -H_{\mathrm{Hom}} \rangle$ from perturbation theory to obtain

$$\langle -\mathcal{H}_{\mathrm{Hom}} \rangle \propto z^0{}_{\mathrm{Hom}} + O[(z^0{}_{\mathrm{Hom}})^2]; \qquad |z^0{}_{\mathrm{Hom}}| \ll 1 \qquad \text{(B.16)}$$

and for $|z^0{}_{\mathrm{Hom}}| \ll 1$, we know that our characteristic length ξ_{Hom} of the confined chain must scale as

$$\xi^2{}_{\mathrm{Hom}} \sim \langle \mathbf{R}^2 \rangle_{0f} \sim n, \qquad |z^0{}_{\mathrm{Hom}}| \ll 1, \quad \nu = 1/2 \qquad \text{(B.17)}$$

in accord with the physical situation that the chain is almost unbound. Eliminating $\langle -\mathcal{H}_{\mathrm{Hom}} \rangle$ from (B.15) and (B.16) we infer $E_0 \sim n^{\phi_{\mathrm{Hom}}-1}$. From (B.17) and (B.14) we conclude the limiting relations between ξ_{Hom} and E_0 in the weak and strong localization regimes as

$$\xi^2{}_{\mathrm{Hom}} \sim E_0{}^{1/(\phi_{\mathrm{Hom}}-1)}, \qquad |z^0{}_{\mathrm{Hom}}| \ll 1, \quad 0 < \phi_{\mathrm{Hom}} < 1 \qquad \text{(B.18a)}$$

$$\xi^2{}_{\mathrm{Hom}} \sim E_0{}^{-1}, \qquad |z^0{}_{\mathrm{Hom}}| \gg 1 \qquad \text{(B.18b)}$$

The first expression does not seem to have been noted before. We see that homogeneous potentials not only exhibit a universal strong confinement behavior but also exhibit universal behavior at the localization–delocalization transition, $|z^0{}_{\mathrm{Hom}}| \lesssim 1$. An interesting special case of (B.18) corresponds to $\phi_{\mathrm{Hom}} = \phi_2 = \epsilon/2$, which is relevant[9] to polymer collapse and electron localization in disordered materials due to the presence of dense random impurities. Equations B.18a and B.18b become $(0 < \phi_2 < 1)$, $d_{\mathrm{fc}} = 2$

$$\xi_{\mathrm{Hom}} \sim |E - E_{\mathrm{c}}|^{-1/(d-2)} \qquad \text{(weak localization; } E \approx E_{\mathrm{c}}) \qquad \text{(B.19a)}$$

$$\xi_{\mathrm{Hom}} \sim |E - E_{\mathrm{c}}|^{-1/2} \qquad \text{(strong localization; } E \ll E_{\mathrm{c}}) \qquad \text{(B.19b)}$$

where $E_0 = E - E_{\mathrm{c}}$ is measured relative to some "edge" E_{c} value corresponding to a transition point where the polymer or electron (or what have you) changes from being localized to being delocalized.[14,44] The E_{c} term is generated typically by the "self-term" of the many-body interaction.[45]

Finally it must be confessed that application of the Kac invariance principle is dangerous in certain instances. The relation only applies to a restricted class of "one-body" potentials depending on a single coordinate $\mathbf{R}(\tau)$ [see (B.1)]. This is not the case for many-body potentials such as those involved in polymer excluded volume and localization by random impurities. The danger is highlighted by the many-body potential considered by Donsker and Varadhan,[46] corresponding to diffusion in a field of random impurities whose density is not restricted to be high. The limiting form of the partition function for this many-body potential is *not consistent with the Kac invariance principle*. On the other hand the potential of Donsker and Varadhan cannot be written in the form (B.1). Use of the Kac invariance principle presumes that it is possible to model the collective many-body interactions of an interacting polymer by a one-body effective potential. Even if the relation lacks exact justification, it seems to "work" in many situations, however. A failure of the Kac invariance principle to hold brings into question the classical mean-field methods based on the ground-state dominant approximation (see de Gennes[42]).

It is also warned that any potential leading to a negative crossover exponent ϕ_{Hom} should be treated with great care.[47] In this instance a finite bound-state energy may not exist and this is reflected in divergent perturbation expansions in $z^0{}_{\mathrm{Hom}}$. The value of $h = 1/d_{\mathrm{fc}}$ [see (B.3c)] is a critical homogeneity power below which the potential may lead to a singular perturbation. For quantum mechanics, where $d_{\mathrm{fc}} = 2$ is the relevant situation, $h = -2$ is known to be "critical" for power law potentials. As a rule of thumb confine attention to a crossover exponent ϕ_{Hom} between 0 and 1. Otherwise beware!

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to order ϵ (see ref 5 also). A comparison is also made with RG calculations for a polymer terminally attached to an impenetrable two-dimensional interface. Analytic predictions are compared with Monte Carlo data. Comparison between the constraint of a polymer in a diblock copolymer and terminally attached to an interface shows semiquantitatively the same trends when the interblock interaction is equated with the polymer surface interaction.

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(30) There is some danger in replacing the surface dimension with the Hausdorff (fractal) dimension and there are instances where the procedure has been shown to be incorrect. Berry (Berry, M. *Proc. Symp. Pure Math.* **1980**, *36*, 13) conjectured a generalization of Weyl's classic result on the asymptotic density of the eigenvalue spectra characterizing the frequencies of vibrating regions as a function of the dimension of the region and the dimension of the boundary. Brossard and Carmona (Brossard, J.; Carmona, R. *Commun. Math. Phys.* **1986**, *104*, 103) have disproved the "identification" of the surface boundary dimension with the Hausdorff dimension of a region having a fractal boundary. However, a more recent calculation by Lapidus and Fleckinger-Pellê (Lapidus, M.; Fleckinger-Pellê, J. *Comp. Rend. Acad. Sci.* (*Paris*) **1988**, *306*, 171) shows that Berry's conjecture is correct *provided* the fractal dimension is equated with the Minkowski fractal dimension rather than the Hausdorff dimension. See also: Stewart, J. *Nature* (*London*) **1988**, *333*, 206. Rammal, R. *J. Phys.* (*Les Ulis, Fr.*) **1984**, *45*, 191. As a final note, it is mentioned that the scaling arguments of Stella for the free energy of a surface-interacting polymer closely parallel the arguments of Berry. This should not be surprising given Kac's well-known derivation[40] of Weyl's theorem from the polymer partition function using the principle of "not feeling the boundary". In conclusion the term "fractal dimension" is used in a loose generic sense indicated by Mandelbrot until a better understanding is obtained of which fractal dimension is really appropriate in a specific application. See: Le Guillou, J. C.; Zinn-Justin, J. *J. Phys.* (*Les Ulis, Fr.*) **1987**, *48*, 19.

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Effect of Polymer Chain Microstructure on Solvent Crystallization: Implications on Polymer Solvation and on Physical Gelation

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ABSTRACT: In this paper we determine by means of the solvent crystallization method the degree of polymer solvation through the parameter $\bar{\alpha}$, which is the average number of solvent molecules per monomer. For polymers possessing side groups such as poly(methyl methacrylate), poly(hexyl methacrylate), and polystyrene there is a simple relation between $\bar{\alpha}$ and the solvent size. For polymers without side groups such as poly(dimethylsiloxane) or poly(vinyl chloride) there is no relation. These results are interpreted with the notion of a cavity formed by the side groups. Temperature–concentration phase diagrams are established for the different polymers in *p*-chlorotoluene. Departures from theoretical solvent melting point depression (Flory) are also accounted for by the notion of cavity. The cavity's effect is examined as to its relevance for understanding the physical gelation of polymers possessing side groups.

Introduction

The interactions between a polymer and a solvent have been and still are widely studied. They constitute an important chapter in the study of amorphous polymer solutions.[1–4]

These interactions also play an important role when crystallizable polymers are dealt with. For instance poly(ethylene oxide) (PEO) can crystallize from solutions either under an "anhydrous" form or under a "solvated" form.[5,6] In the case of PEO–para-disubstituted benzene mixtures, Point et al.[7] have shown that a polymer–solvent compound is produced rather than the "anhydrous" form. According to Point et al.[7] this is so because the solvent molecule adapts perfectly within the shape of the helical form adopted by the polymer. As a result, the compound melts at a temperature higher than that of either component. Similar conclusions have been drawn for syndiotactic poly(methyl methacrylate) (sPMMA).[8]

The same mechanism is thought to occur in physical gelation of stereoregular polymers.[9–11] In this respect, the case of isotactic polystyrene/*cis*-decalin gels is worth mentioning since it has been deeply investigated by different techniques. The temperature–concentration phase diagrams[12] show that gelation arises from the formation of a congruently melting polymer–solvent compound. From neutron diffraction experiments,[11] it is concluded that the compound owes its formation to the cavities formed by the benzene rings: solvent molecules that can enter these cavities can form physical bridges between different chains. The same conclusion is drawn from the study of the solvent crystallization behavior once the gel is produced.[11] A relation has been established between the degree of solvation and the molecular size.

The purpose of this paper is manifold and aims particularly at (i) testing more deeply the reliability of the solvent crystallization method,[11,13] (ii) cross-examining the notion of cavity with other polymers possessing or not possessing bulky side groups, (iii) investigating the problem on a theoretical basis, and (iv) assessing the role of the cavity in the phenomenon of thermoreversible gelation.

As with isotactic polystyrene,[11] we shall examine these points by studying the solvent melting behavior in various types of polymer–solvent mixtures including stereoregular and stereoirregular polymers.

Theoretical Section

1. Polymer–Solvent Phase Diagrams. Whether a polymer is crystallizable or not, different phase diagrams can be obtained as described, in detail, by Pakpov.[14]

(a) If the polymer is liable to crystallize, two schematic types of phase diagrams can be obtained: (i) the polymer crystallizes under an "anhydrous" form which entails rejection of the solvent into the amorphous part leading to the formation of a solid solution (Figure 1a); (ii) the polymer and the solvent cocrystallize so as to form a polymer–solvent compound that melts either congruently or incongruently (Figure 1b).

In both cases, C_{E} represents the concentration at which an eutectic mixture is formed between the solvent and the crystallized polymer (Figure 1a) or the solvent and the polymer–solvent compound (Figure 1b). In this paper we consider situations where the discrepancy between the melting point of either the polymer or the polymer–solvent compound, on the one hand, and the solvent, on the other hand, is large (over 100 °C). Consequently, and as was experimentally shown for oligomers,[15,16] the eutectic concentration C_{E} is shifted toward zero, which entails a merge

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