Adsorption onto the surface of a random heteropolymer chain

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Near the adsorption point, polymer chains with different random monomer sequences begin to acquire very different configurational properties over distances $N \sim e^{1/\Delta}$, where Δ is a measure of the dispersion of the energy of the interaction with the surface (in units of kT) of the monomers of the various species. Expressions are derived for the distribution function of the monomers near the surface and for the moments of this distribution, averaged over all possible sequences. Expressions are also derived for the dispersion of these quantities. Over distances $N \gg e^{1/\Delta}$ these expressions are universal in the sense that they do not depend on the parameter Δ, which characterizes the inhomogeneity. If the fractal dimensionality of the adsorbing surface is greater than 2 (if the surface is rough, if there are pores, etc.) the length scale will be determined by a power-law, rather than exponential, dependence. The three-dimensional interaction of the monomers generally enhances the effects caused by the heterogeneous nature of the chain.

1. INTRODUCTION

The adsorption of a polymer chain is one of the classic problems in polymer physics. Its importance stems from the circumstance that the adsorption transition is similar in many ways to coil-globule transitions, which are the basic types of conformational transitions in linear polymers. Associated with these transitions are many aspects of the functioning of polymers in living organisms and many technological applications. Many chromatographic methods for studying polymers have been developed on the basis of these transitions. Although numerous theoretical papers have been published on adsorption (see the review by Binder[1]) and on the coil-globule transition (see the reviews by Lifshits *et al.*[2] and Grosberg and Khokhlov[3]), these papers have been restricted to a study of so-called homogeneous linear polymers. This term is applied to polymers which consist of monomers of a single species or of a sequence of monomers of different species which is repeated many times, e.g., *A-B-C–A-A-B-C–A-B-C–*. . . . In nature, on the other hand, the vast majority of polymers—DNA molecules and protein molecules—are aperiodic. Correlation analysis of such sequences reveals no large-scale regular behavior of any sort in them. This conclusion means that knowledge of the first n terms is of no help in predicting the $(n+1)$st term. In other words, from the statistical standpoint such sequences may be regarded as a realization of a random process.

One might ask whether coil-globule phase transitions and adsorption transitions occur in the same way as for some homogeneous polymer with average characteristics or whether distinctive individual features arise for each random polymer sequence and persist in the limit $N \to \infty$. In a previous study[4] we showed that the critical dimensionality of the space for the coil-globule transition is $d_c = 3$. For $d > 3$, the geometric and thermodynamic characteristics of a random heteropolymer are self-averaged as $N \to \infty$. For $d \leqslant 3$, any arbitrarily small inhomogeneity gives rise to a relative dispersion ~ 1 in the values of observable quantities in the transition region at a large scale.

A corresponding situation arises for the adsorption transition. We denote by d' the dimensionality of the entity on which the adsorption occurs. Thus $d' = 2$ would correspond to the adsorption of a polymer on a plane, $d' = 1$ to adsorption of a polymer on a line, and $d' = 0$ to adsorption on a point.[1)] There can also be cases in which the dimensionality d' is not an integer. For example, if the adsorption occurs at the inner surface of a porous material or on a highly irregular surface then such a surface could be characterized by a fractal dimensionality d' in the interval $3 > d' > 2$. We will show below that $d' \geqslant 2$, i.e., in the situations which are physically most realistic, no self-averaging of observable quantities occurs at the adsorption point of a random heteropolymer.

The relative dispersion in observable quantities for different random sequences of monomers increases with the length of the polymer chains, and at a a certain scale it reaches a value on the order of unity. The substitution of one single monomer or the interchange of monomers in a chain affects the observable quantities characterizing the given chain to a far greater extent than the corresponding substitution in a homogeneous polymer would. The three-dimensional interaction of monomers amplifies these effects.

The adsorption transition, like the coil-globule transition, can therefore be used as a sensitive mechanism for separating heteropolymers with different sequences of monomers. In a living cell a mechanism operates to select certain protein sequences by comparing these sequences with a complementary matrix. (This is essentially again the adsorption of a heteropolymer, but on the complementary polymer molecule, rather than on a surface. This transition is distinguished in several important ways from the transition with which we are concerned in the present paper; in particular, fluctuation effects are important only at short range.[5]) The mechanism for the separation of polymer sequences which we are proposing here differs from the mechanism which operates in a living cell because it involves the collective interaction of many monomers. It is thus a more global and less single-valued mechanism. On the other hand, the mechanism which we are proposing here is substantially simpler, and it makes possible a separation in a large mass of polymer chains simultaneously.

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2. DESCRIPTION OF THE MODEL; DIMENSIONALITY ESTIMATES

Since we are interested in the properties of long chains, for which many details of the microscopic structure are unimportant, we consider a simplified model of a polymer chain: as a chain consisting of small spheres or beads of different species, connected in series by flexible bonds of identical length[2)] (Fig. 1). We assume that the beads differ only in the energy w_i of their interaction with the adsorbing wall, and for the time being we will ignore the interaction of the beads with each other in space. We take up the effects of three-dimensional interaction at the end of the paper. We assume that the sequence of beads of different species along the chain is random.

Let us briefly review results on the problem of the adsorption at a wall of a homogeneous chain without three-dimensional interactions for the case in which one end of the chain is fixed to the wall. It is not difficult that this problem is equivalent to that of adsorption on a permeable "attracting plane" (Fig. 2). Although this problem has been solved exactly,[6] we will content ourselves with some dimensionality estimates here. Specifically, with any configuration of the chain which arises in the problem of adsorption on a permeable plane we can associate a configuration from the problem of adsorption on a impermeable wall, which can be found through mirror reflection through the permeable plane of the part of the polymer coil in the left-hand half-space. We can do this only if we ignore the spatial interaction energies of the two parts of the polymer coil which coincide in the right-hand half-space, i.e., only if we assume an ideal polymer chain. To each configuration of the problem of adsorption on a wall correspond 2^N configurations from the problem of adsorption on a permeable plane, where N is the number of adsorbed monomers.

In order to deal with the difference in configurational entropies, we must require that the adsorption energy of a single monomer in the problem of adsorption on a wall be smaller by $kT \ln 2$ than the corresponding energy in the problem of adsorption on a permeable plane.[3)] In the latter problem, the adsorption point is obviously $w_a = 0$; at this point the polymer coil is purely Gaussian (Fig. 2a), and we have $\langle R^2 \rangle \sim N$. The average density of monomers in the coil is $\rho \sim N/R^3$ and there are a total of $\rho R^2 \sim N^{1/2}$ monomers in the adsorbing plane.

If $w \neq 0$, the total energy of the interaction of the coil with the surface is on the order of $|w|N^{1/2}$. If this energy is smaller than kT, the wall has little effect on the Gaussian nature of the structure of the coil. If $|w|N^{1/2} > kT$, the structure of the coil changes. We partition the polymer chain into regions of length m (blobs) in such a way that we have $|w|m^{1/2} \approx kT$. At scales smaller than $r^* \approx m^{1/2}$, the chain can then be treated as Gaussian again, but as we increase the scale of the treatment in units of blobs of length scale r^* the chain becomes completely desorbed or adsorbed, depending on the sign of w.

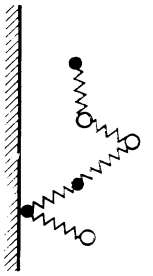

FIG. 1. Model of a heteropolymer as a chain consisting of beads of different species connected by flexible bonds of identical length.

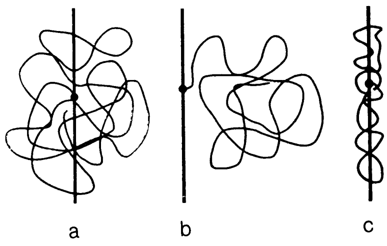

FIG. 2. Adsorption of a homogeneous polymer chain with one end fixed on a permeable plane. a—$w = 0$ is the adsorption point; b—$w > 0$ is a desorbed state; c—$w < 0$ is an adsorbed state.

For the polymer chain as a whole, the adsorption transition occurs in a narrow interval of adsorption energies, $\sim kT/N^{1/2}$, or of temperatures, $\sim T/N^{1/2}$. (We recall that the adsorption point in the problem with an impermeable wall is $w_a = -kT \ln 2$, and this point may be passed as the temperature changes. We will replace the two variables T and w by the single variable w, assuming $kT = 1$.)

If the adsorption occurs on a surface with a fractal dimensionality d', the number of monomers of a Gaussian polymer coil on the adsorbing surface at the adsorption point is

$$\mathcal{N} = \rho R^{d'} = N^{\varphi}, \qquad \varphi = (d'-1)/2. \tag{1}$$

The width of the adsorption transition is determined in this case by the relation

$$|w| < \mathcal{N}^{-1} = N^{(1-d')/2}. \tag{2}$$

We now return to the problem of an inhomogeneous chain consisting of a random sequence of monomers with a desorption energies $w \pm \Delta w$. According to the estimates above, over length scales smaller than the correlation length,

$$r^* \sim |w|^{1/(1-d')}, \tag{3}$$

all the monomers of a selection of the chain participate in the adsorption identically. The number of such monomers is $m \sim (r^*)^2$. Since the composition of this section of the chain is random, the numbers of monomers of the different species are not exactly equal to each other; they differ by amounts $\sim m^{1/2}$. The average adsorption energy per monomer in this section of the chain is [see (2)]

$$w + \Delta w O(m^{-1/2}) = w\,[1 + \Delta w O(w^{(2-d')/(d'-1)})] \quad (m < N).$$

It follows from this estimate that for $d' > 2$ the relative magnitude of the correction for the inhomogeneity diverges at the adsorption point (as $w \to 0$). This statement means that for a long polymer ($N \to \infty$) and for small values of w the leading role is played not by the general attraction or repulsion but by effects which arise from the inhomogeneity of the chain. Let us estimate the chain length n_c and the length scale $r_c \sim n_c^{1/2}$, over which effects due to the inhomogeneity reach a magnitude of order unity in the case $w = 0$. Replacing w by $\Delta w n_c^{-1/2}$, in estimate (3) of the correlation length, we find

$$r_c \sim n_c^{1/2} \sim (\Delta w)^{-1/(d'-2)}. \tag{4}$$

At the adsorption point in the case $d' > 2$ the polymer chain can thus be partitioned into sections of length n_c for each of which either an adsorption condition or a desorption holds. With $d' = 2$, as we will see below, the situation is logarithmic, and the length scale n_c depends on Δw exponentially, rather than in accordance with a power law.

The balance of this paper is ordered in the following way. We are focusing primarily on the case of adsorption on a plane ($d' = 2$). In the following section of the paper we derive and solve an equation for the probability for the adsorption of an nth monomer of a random polymer chain as a function of the probability for the adsorption of all preceding monomers. We then derive an expression for quantities averaged over all possible polymer sequences and also for the dispersion in these quantities.

We then take up the question of the sensitivity of the measured quantities for some specific chain to a substitution of an arbitrary monomer by a monomer of another species and to the interchange of two adjacent monomers. We also examine the case of an absorbing surface of arbitrary fractal dimensionality $d' > 2$. We conclude with a discussion of the role played by effects of the three-dimensional interaction of monomers.

3. ADSORPTION ON A PLANE; DERIVATION OF THE BASIC EQUATIONS

For a homogeneous polymer chain, the adsorption problem is solved in principle once we know its partition function $Z(r_0, r_N)$ near the $z = 0$ surface, where r_0 and r_N are the coordinates of the ends of the chain [$r = (x,y,z)$]. In terms of this partition function we can express the two quantities which are used most frequently: the spatial distribution of the ends of the chain,

$$\mathscr{G}(r_0, r_N) = Z(r_0, r_N) \Big/ \int\int Z(r_0', r_N')\, dr_0'\, dr_N', \tag{5}$$

and the conditional probability for finding one end of the chain at point r_N if the other end is fixed at r_0,

$$G(r_0, r_N) = Z(r_0, r_N) \Big/ \int Z(r_0, r_N')\, dr_N'. \tag{6}$$

A much more complicated problem is that of a random polymer chain; for example, the problem of taking an average of the quantities in (5) and (6) over different sequences generally are different problems. In an integration over space, the state of the molecule near the surface and far from it thus contribute to the denominator in (5). For these states, the inhomogeneity of the polymer chain is inconsequential, and if these states dominate the integral the averaging of (5) reduces to finding the average value of the numerator in (5), i.e., the average value of the partition function $Z(r_0, r_N)$.

In the absence of three-dimensional interactions, the average over inhomogeneities can be carried out independently for each link of the polymer chain. Accordingly, the average of the partition function is equal to the partition function of a homogeneous polymer chain with the average adsorption energy. In this case it is a simple matter to derive expressions for all averages of observable quantities; they are expressed in terms of correlation function (5).

In taking the average in (6) we need to simultaneously average the numerator and the denominator, including the cross terms. As we will see below, the basic difficulty here is in dealing with the divergent logarithmic terms. [The same difficulty arises in the course of the averaging in (5) if the geometry of the problem is such that the relative number of surface states in the denominator in (5) is comparable to the contribution from the integration over the entire space. It is thus necessary to impose the relation $V \gtrsim RS$, where V is the volume of the system, S is the area of the adsorbing surface, and R is the length scale of the polymer coil.]

We will use a recurrence-equation method here. This method yields results which are more detailed than those found by the renormalization-group method, in particular for asymptotically long polymer chains. For simplicity we assume that the first monomer is pinned to the surface: $G_0(z) = \delta(z)$. We omit the dependence of G_n on the coordinates x and y, since this dependence is described by the random-walk correlation functions

$$G_n(x_n - x_0) = E_n(x_n - x_0), \qquad G_n(y_n - y_0) = E_n(y_n - y_0),$$

$$E_n(\zeta) = \pi^{-1/2} n^{-1/2} e^{-\zeta^2/n}.$$

We assume that $G_n(z)$ is the distribution function of the nth monomer. The normalized distribution function of the next monomer, is then

$$G_{n+1}(z) = \pi_{n+1}(z) \Big/ \int \pi_{n+1}(z')\, dz', \tag{7}$$

$$\pi_{n+1}(z) = \int G_n(z-z') E_1(z')\, dz' + \delta(z)\,(e^{-w_{n+1}} - 1) \cdot \int G_n(z') E(z')\, dz'. \tag{8}$$

(Here and below, the integration over z runs from $-\infty$ to $+\infty$.) Expanding the numerator and denominator in (7) in powers of w_{n+1}, and retaining terms of up to second order, we find

$$G_{n+1}(z) = \int G_n(z-z') E_1(z')\, dz' \left[1 + \left(w_{n+1} - \frac{w_{n+1}^2}{2}\right)\lambda_n - w_{n+1}^2 \lambda_n^2\right] - \left[\left(w_{n+1} - \frac{w_{n+1}}{2}\right)\lambda_n - w_{n+1}^2 \lambda_n^2\right] \delta(z), \tag{9}$$

where

$$\lambda_n = \int G_{n-1}(z') E_1(z')\, dz' \sim n^{-1/2}. \tag{10}$$

If all the monomers are identical, the value $w = 0$ corresponds to the adsorption point. In this case the coefficients of all powers of λ_n vanish. We then have $G_n(z) = E_n(z)$. For $w > 0$ and $w < 0$, the most important corrections arise from terms which are linear in λ_n. With increasing n, these corrections accumulate, and they change the solution substantially at $n \sim |w|^{-2}$ (cf. the estimates of the preceding section). If there is dispersion in the interactions, the adsorption point—i.e., the point at which the terms linear in λ_n vanish—shifts slightly: $w_a = \overline{w}^2/2$. We will use this value as the origin of the scale for the random quantities w_n: $\overline{w}_n = 0$.

Our basic problems in this section of the paper are to reduce the functional equation (9) for $G_n(z)$ to a closed equation for $G_n(z)$ which incorporates only the values of the function $G_{n'}(z)$ at $z=0$ for all preceding $n'<n$ and to analyze this equation. Since the correspondence between the equations is one-to-one, we will derive expressions for the most interesting measurable quantities and their dispersion from the equation which we find.

In the unaveraged recurrence equation we switch to the momentum representation:

$$G_n(k)=\int G_n(z)e^{ikz}\,dz.$$

We write the function $G_n(k)$ as the product of two functions, explicitly identifying out Gaussian and random components:

$$G_n(k)=\Phi_n(k)E_n(k)\qquad (E_n(k)=e^{-nk^2/4}). \tag{11}$$

For $\Phi_n(k)$ we find

$$\Phi_n(k)=\Phi_{n-1}(k)(1+w_n\lambda_n+w_n^2\lambda_n^2)-(w_n\lambda_n+w_n^2\lambda_n^2)e^{nk^2/4}, \tag{12}$$

where

$$\lambda_n=\int\Phi_{n-1}(k)E_n(k)\frac{dk}{2\pi}. \tag{13}$$

Expanding $\Phi_n(k)$ in a series in powers of $nk^2/4$,

$$\Phi_n(k)=\sum_{l=0}^{\infty}\frac{a_n^l}{l!}\left(\frac{nk^2}{4}\right)^l\qquad (a_n^0\equiv1), \tag{14}$$

we find a system of equations for the coefficients a_n^l:

$$a_n^l=[(n-1)/n]^l a_{n-1}^l(1+w_n\lambda_n+w_n^2\lambda_n^2)-(w_n\lambda_n+w_n^2\lambda_n^2). \tag{15}$$

The coefficient a_n^l thus depend only on $w_{n'}$ and $\lambda_{n'}$, $n'\leqslant n$:

$$a_n^l=-\sum_{n'=1}^{n}(w_{n'}\lambda_{n'}+w_{n'}^2\lambda_{n'}^2)\left(\frac{n'}{n}\right)^l$$

$$\cdot\exp\left\{\sum_{n''=n'+1}^{n}(w_{n''}\lambda_{n''}+w_{n''}^2\lambda_{n''}^2)\right\}. \tag{16}$$

Substituting (14) into (13), we can express λ_n in terms of a_{n-1}^l:

$$n^{1/2}\lambda_n=1+\sum_{l=1}^{\infty}\frac{(2l)!}{l!\,l!\,2^{2l}}a_{n-1}^l. \tag{17}$$

Finally substituting (16) into (17), and summing over λ, we find

$$\varepsilon_n=1-\sum_{n'=1}^{n-1}\left(\frac{w_{n'}\varepsilon_{n'}}{(n-n')^{1/2}}+\frac{w_{n'}^2\varepsilon_{n'}^2}{n^{1/2}(n-n')^{1/2}}\right)$$

$$\cdot M\left(\frac{n'}{n}\right)\exp\left\{\sum_{n''=n'+1}^{n}\left[w_{n''}\frac{\varepsilon_{n''}}{(n'')^{1/2}}+w_{n''}^2\frac{\varepsilon_{n''}^2}{n''}\right]\right\}, \tag{18}$$

where

$$M\left(\frac{n'}{n}\right)\equiv\sum_{l=1}^{\infty}\frac{(2l)!}{l!\,l!\,2^{2l}}\left(\frac{n'}{n}\right)^l\left(\frac{n}{n'}-1\right)^{1/2}$$

$$\approx1\qquad\text{for}\qquad n-n'\ll n.$$

Here we have introduced some new notation: $\varepsilon_n\equiv\lambda_n n^{1/2}$ (for a Gaussian chain we would have $\varepsilon_n=1$). In the expression in parentheses in (18) we first restrict the analysis to the term which is linear in ε. The factor $(n-n')^{-1/2}$ means that ε_n will be affected most by the nearest monomers with $n-n'\ll n$, for which we can ignore the exponential factor in (18). The factor $M(n'/n)$ can also be replaced by unity. We can then write the following simplified version of Eq. (18):

$$\varepsilon_n=1-\sum_{n'=1}^{n-1}\frac{w_{n'}\varepsilon_{n'}}{(n-n')^{1/2}}. \tag{18'}$$

It is thus possible to reduce the functional recurrence equation (9) to an equation containing only the values of the function at the point $z=0$ for different values of n'. This is not a Markov equation, and it does not reduce to a Markov process. The most important problem, as we will see below is the behavior of Eq. (18′) in the limit $\varepsilon_n\gg1$; the following random quantity w_n may then change ε_{n+1} greatly. In this case we ignore the one on the right side of (18), and we find that the fluctuating quantity is not ε but more precisely $\ln\varepsilon$ [see (23) below]. Physically, the condition $\varepsilon_n\gg1$ corresponds to the case in which the attracting monomers are positioned in the polymer sequence in such a way that the probability for finding the next monomer at the surface is far greater than that in the Gaussian case. Each successive monomer which we add will thus have a substantial effect on the configurational statistics of the chain, depending on whether it is attractive or repulsive.

Let us find the distribution function $f(\varepsilon_n)$ for the ensemble of all different polymer sequences. We can do this by calculating the moments of the distribution function:

$$\overline{\varepsilon_n^m}=\int_0^\infty\varepsilon_n^m f(\varepsilon_n)\,d\varepsilon_n.$$

In our approximation we evidently have $\bar{\varepsilon}_n=1$. Squaring (18′), and taking an average over w_i, we find

$$\overline{\varepsilon_n^2}=1+\sum_{m=1}^{n-1}\overline{\varepsilon_{n-m}^2}\frac{\Delta}{m}. \tag{19}$$

To solve this equation, we multiply (19) by $e^{-\tau n}$ and sum over n:

$$\overline{\varepsilon_\tau^2}=\frac{1}{\tau}+\sum_m\overline{\varepsilon_\tau^2}\frac{\Delta}{m}e^{-\tau m}. \tag{20}$$

We then find

$$\overline{\varepsilon_\tau^2}=\frac{1/\tau}{1-\Delta\ln(1/\tau)}.$$

Taking inverse Laplace transforms, we find

$$\overline{\varepsilon_n^2}=\frac{1}{1-\Delta\ln n}\qquad(n\ll n_c), \tag{21a}$$

$$\overline{\varepsilon_n^2}=\frac{1}{\Delta}e^{n/n_c}\qquad(n\gg n_c\equiv e^{\Delta}). \tag{21b}$$

Analogous calculations for the higher-order moments $\overline{\bar{\varepsilon}_n^{1/2}}$ yield

$$\overline{\varepsilon_n^m}=[(1-\Delta\ln n)^{m(m-1)/2}]^{-1}\qquad(n\ll n_c). \tag{22}$$

In contrast with (21), which was derived with a "ladder" accuracy, and which allows an analytic continuation at $n > n_c$, expression (22) was derived with a "parquet" accuracy and is valid only under the condition $1 - \Delta \ln n > \Delta$. Expressions (21) and (22) unambiguously determine the form of the function $f(\varepsilon_n)$ for $\varepsilon > 1$ and $1 - \Delta \ln n > \Delta$:

$$f(\varepsilon_n)\,d\varepsilon_n = \pi^{-1/2}\omega^{-1}\exp\left(-\frac{\ln^2\varepsilon_n}{\omega^2} - \frac{\ln\varepsilon_n}{2} - \frac{\omega^2}{16}\right)d\ln\varepsilon_n, \tag{23}$$

where

$$\omega^2 = 2\ln(1-\Delta\ln n)^{-1}.$$

We can conclude from the form of expression (21) for $\overline{\varepsilon_n^2}$ that for $n \geqslant n_c$ the dispersion of distribution function (23) does not diverge, and there is instead a transition to exponential growth: $\omega^2 \sim e^{n/n_c}$. The nonlinear term in (18) obviously becomes important in this case; it limits the growth of sequences with large value of ε. We take an average of (18):

$$\overline{\varepsilon}_n = 1 - \sum_{n'=1}^{n-1} M\left(\frac{n'}{n}\right)\overline{\frac{\Delta\varepsilon_{n'}^2}{n^{1/2}(n-n')^{1/2}}\gamma},$$
$$\gamma = \exp\sum_{n''=n'+1}^{n}\frac{\Delta\varepsilon_{n''}^2}{n''}. \tag{24}$$

It follows from the physical condition that the adsorption probability be positive ($\overline{\lambda_n} > 0$ and $\overline{\varepsilon}_n > 0$) that the absolute value of the second term on the right side of (24) must not exceed unity. It can be shown that in the asymptotic region this absolute value approaches unity, and we have $\overline{\varepsilon}_n \to 0$. Specifically, if $\overline{\varepsilon}_n$ tends not toward zero but toward some nonzero value, then we conclude that $\overline{\varepsilon_n^2}$ increases without bound, as in (19)-(21). Actually, there is an upper bound on $\overline{\varepsilon_n^2}$, and its limiting value can be found from (24) by setting $\lim_{n\to\infty}\overline{\varepsilon}_n = 0$. If we ignore terms on the order of n_c/n, we can uncouple the averaging processes in the exponential function in (24):

$$\sum_{l=1}^{\infty}\frac{(2l)!}{l!\,l!\,2^{2l}}\frac{\Delta\overline{\varepsilon_n^2}}{l-\Delta\overline{\varepsilon_n^2}} = 1.$$

A numerical solution of this equation yields

$$\Delta\overline{\varepsilon_n^2} = 0.505\ldots. \tag{25}$$

The behavior of ε_n and $n > n_c$ can be described as fluctuations between zero and a value on the order of $1/\Delta$, in which the nonlinearity "rolls up" the sequence ε_n to small values of ε. The ε_n are concentrated near zero for the most part, and excursions $\sim 1/\Delta$ which contribute to the dispersion (25) are comparatively rare.

4. AVERAGE VALUES OF OBSERVABLE QUANTITIES AND THEIR DISPERSION FOR POLYMER CHAINS WITH DIFFERENT SEQUENCES OF MONOMERS

In this section we derive an expression for the moments of the spatial distribution function of n monomer chain of n units:

$$\langle z^{2m}\rangle = \int z^{2m}G_n(z)\,dz.$$

We substitute (16) and (14) into (11), ignoring the exponential term in (16):

$$\langle z^{2m}\rangle = \frac{\partial^{2m}}{\partial k^{2m}}G(k)\Big|_{k=0} = \frac{n^m}{2^{2m}}\frac{(2m)!}{m!}\Bigg[1+\sum_{n'=1}^{n}(w_{n'}\lambda_{n'} + w_{n'}^2\lambda_{n'}^2)\left(1-\frac{n-n'}{n}\right)^m \exp\sum_{n''=n'+1}^{n}(w_{n''}\lambda_{n''}+w_{n''}^2\lambda_{n''}^2)\Bigg]. \tag{26}$$

Taking an average over all possible sequences of monomers, we find

$$\overline{\langle z^{2m}\rangle} = \frac{n^m}{2^{2m}}\frac{(2m)!}{m!}\left[1-\sum_{l=1}^{m}(-1)^l\frac{\Delta\overline{\varepsilon_n^2}}{l-\Delta\overline{\varepsilon_n^2}}\frac{m!}{l!\,(m-l)!}\right]. \tag{27}$$

For a chain of length less than n_c, we can use expression (21) for ε_n^2; for asymptotically long chains we can use expression (25) and in this case the average values of the moments are universal quantities,[4)] which do not depend on Δ:

$$\langle\overline{z^2}\rangle = c_2 n, \quad \langle\overline{z^4}\rangle = c_4 n^2, \ldots,$$
$$c_2 = 1{,}01\ldots\,(^1/_2), \quad c_4 = 2{,}02\ldots\,(^3/_4), \ldots. \tag{28}$$

Calculating the dispersion in the quantities $\langle\overline{z^{2m}}\rangle$ for various sequences of monomers, we find

$$\mathscr{D}(\langle z^{2m}\rangle) = \overline{\langle z^{2m}\rangle^2} - \langle\overline{z^{2m}}\rangle^2 = \left(\frac{n^m(2m)!}{2^{2m}m!}\right)^2 \cdot\left\{2\sum_{l=1}^{m}\frac{(-1)^l}{l-\Delta\overline{\varepsilon_n^2}}\frac{m!}{l!\,(m-l)!} - \sum_{l'=1}^{2m}\frac{(-1)^{l'}}{l'-\Delta\overline{\varepsilon_n^2}}\frac{2m!}{l'!\,(2m-l')!}\right\}\Delta\overline{\varepsilon_n^2}. \tag{29}$$

For asymptotically long chains, the dispersion of the observable quantities is also universal:

$$\mathscr{D}(\langle z^2\rangle) = 0{,}084\ldots n^2, \qquad \mathscr{D}(\langle z^4\rangle) = 0{,}38\ldots n^2, \ldots. \tag{30}$$

We can calculate the changes in measurable quantities, e.g., $\langle z^2\rangle$, when a single monomer at an arbitrary t in the chain is replaced. We vary (26) with respect to the adsorption energy of the tth monomer. Retaining only the terms linear in ε, we find

$$w_t\frac{\delta\langle z^2\rangle}{\delta w_t} = \frac{w_t}{2}\left[\varepsilon_t t^{1/2} + \sum_{t<n'<n} w_{n'}(n')^{1/2}\frac{\delta\varepsilon_{n'}}{\delta w_t}\right]. \tag{31}$$

For a homogeneous polymer chain at the adsorption point, in which case we have $w_i = 0$ for all i except $i = t$, the effect of replacing a single monomer is described by the first term on the right side of (31) with $\varepsilon_t = 1$:

$$w_t\frac{\delta\langle z^2\rangle}{\delta w_t} = w_t\frac{t^{1/2}}{2}. \tag{32}$$

For a disordered chain we need to deal with the change in the adsorption conditions for all successive links. Specifically, the replacement of a single monomer has the consequence that the probability for all successive monomers to be near the adsorption surface changes. These changes alter the magnitude of the contribution of the inhomogeneities of successive monomers to measurable quantities, etc. From Eq. (18), which we restrict to terms linear in ε, we find

$$\frac{\delta\varepsilon_{n'}}{\delta w_t}=-\frac{\varepsilon_t}{(n'-t)^{1/2}}-\sum_{t<n''<n'}\frac{w_{n''}}{(n'-n'')^{1/2}}\frac{\delta\varepsilon_{n''}}{\delta w_t}. \tag{33}$$

It is not difficult to see that logarithmic terms similar to (21a) arise in a calculation of $\overline{(\delta\varepsilon_{n'}/\delta w_t)^2}$:

$$\overline{\left(\frac{\delta\varepsilon_{n'}}{\delta w_t}\right)^2}=\frac{\overline{\varepsilon_t^2}}{n'-t}(1+2\Delta\ln(n'-t)+\ldots). \tag{34}$$

At a large scale, the effect of changes in the adsorption conditions for the other monomers increases and becomes the dominant effect. Remarkably, on the average the sign of this effect (i.e., the decrease or increase in $\langle z^2\rangle$) is not related to the sign of w_t. Over lengths $\sim n_c$, expression (34) reaches its limiting value:

$$\overline{\left(\frac{\delta\varepsilon_{n'}}{\delta w_t}\right)^2}\approx\frac{1}{\Delta^2}\frac{1}{n'-t}. \tag{35}$$

The mean square change $\langle z^2\rangle$ is

$$\overline{\left(w_t\frac{\delta\langle z^2\rangle}{\delta w_t}\right)^2}\approx n. \tag{36}$$

Since we have not considered terms of higher order in ε over scales greater than n_c, an additional factor in the form of an arbitrary function of n_c/n might appear in (36). It is important to note that in any case there will be no dependence on t or on the parameter Δ, which characterizes the inhomogeneity of the chain, in (36).

Similar calculations yield the changes in measurable quantities which stem from the interchange of two neighboring monomers of different species in the chain, say the tth and $(t+1)$st ($w_t=w_{t+1}$). For simplicity we restrict the analysis to an estimate of the effect of such a substitution. The quantities w_t and w_{t+1} appear in all the expressions in the combination

$$\frac{w_t\varepsilon_t}{t^{1/2}}+\frac{w_{t+1}\varepsilon_{t+1}}{(t+1)^{1/2}}\approx\frac{1}{2}\frac{w_t\varepsilon_t}{t^{3/2}}+\frac{w_t}{t^{1/2}}(\varepsilon_t-\varepsilon_{t+1}). \tag{37}$$

For an interchange of monomers, i.e., a change in the sign of w_t, the change in (37) is

$$\frac{1}{t^{1/2}}\left[\frac{w_t}{t}+2w_t\sum_{n'<t}\left(\frac{1}{(n')^{1/2}}-\frac{1}{(n'+1)^{1/2}}\right)w_{t-n'}\right].$$

This change is equivalent to a change in the adsorption energy of a single monomer, say the tth, by the amount given in brackets. After we take an average over all other monomers, we are left with only the first term, w_t/t.

Consequently, the effect of an interchange of monomers is weaker by a factor of t than the effect of a change in the monomer species.

5. THE CASE $d'=2+\varepsilon$

In this section of the paper we consider the case in which the fractal dimensionality of the adsorbing surface is greater than 2. A situation of this sort arises if the adsorbing surface is inhomogeneous and can be described as a fractal of dimensionality $3>d'>2$ over the range of scales from a minimum (atomic) scale to a maximum scale on the order of $r_c\sim n_c^{1/2}$ (an expression for n_c is given below).

In this case we can carry out all the calculations of the two preceding sections, replacing the integration over dz by an integration over a space of dimensionality $3-d'$, i.e., by using $d^{1-\varepsilon}z$. We then replace $\varepsilon_n n^{-1/2}$ by $\varepsilon_n n^{-(1-\varepsilon)/2}$ and $(2l)!/l!2^{2l}$ by $\Gamma[(1-\varepsilon)/2+l]/\Gamma[(1-\varepsilon)/2]$. In place of (18′) we find

$$\varepsilon_n=1-\sum_{n'=1}^{n-1}\frac{w_{n'}\varepsilon_{n'}}{(n-n')^{(1-\epsilon)/2}}. \tag{38}$$

Expressions for $\overline{\varepsilon_n^m}$ at $n<n_c$ are found from (22) by replacing $\Delta\ln n$ by $\Delta(n^\varepsilon-1)/\varepsilon$, $n_c=\exp\Delta^{-1}$ by $(1+\varepsilon/\Delta)^{1/\varepsilon}$, etc.

In the asymptotic region, $n\gg n_c$, we find in place of (25)

$$\overline{\Delta\varepsilon_n^2}=(0.505\ldots+O(\epsilon))/n^\epsilon. \tag{39}$$

It is then not difficult to see that to within terms on the order of ε the expressions for the average moments of the distribution function and their dispersion remain the same as (28) and (30) in the numerical coefficients. We will not reproduce the exact values of these coefficients here since for a surface with large- and small-scale inhomogeneities the procedure of calculating and comparing quantities of the type $\overline{\langle z^2\rangle}$, etc., for homogeneous and inhomogeneous polymer chains is more qualitative than quantitative procedure, which demonstrates the universality (i.e., the lack of Δ dependence) of the asymptotic behavior of inhomogeneous chains.

6. INCORPORATION OF THREE-DIMENSIONAL INTERACTIONS

We need to bear in mind that molecules of different species will generally interact with each other in different ways in three dimensions. If a chain consists of monomers of two species, then there exist three different binary-interaction constants for the monomers: g_{11}, g_{22}, and g_{12}. We can write expressions for these constants by focusing on the average interaction and the deviation from it:

$$g_{ab}=g+u(\mu_a+\mu_b)+v\mu_a\mu_b. \tag{40}$$

Here $\mu_1=1$ and $\mu_2=-1$, so we have $\overline{\mu_a}=0$ and $\overline{\mu_a^2}=1$. We showed previously[4] that if the average interaction of the monomers, g, was nonzero ($|g|>uN^{1/2}$) it would dominate the exchange interaction and would lead to screening of three-dimensional effects from the inhomogeneous part of the interaction. In the adsorption of polymers, it is customary to use a so-called good solvent—one for which the relation $g>0$ holds. Recently, however, interest has been attracted to the use of θ-solvents—for which the relation $g=0$ holds—in adsorption problems, since this approach causes side effects associated with the dispersion in the lengths of the polymer chains (a dispersion which is difficult to eliminate) to drop out of the problem. Let us consider both of these cases.

Adsorption in a good solvent. The effects of polymer-chain inhomogeneity during adsorption and the effects of three-dimensional interactions cannot be taken into account simultaneously within the framework of the recurrence relation (7), since there is an integration over the coordinates of all the preceding monomers in that equation, without consideration of their interaction with the nth monomer. In principle, these calculations can be carried out only with the help of the renormalization-group formalism. Even when that approach is taken, however, some serious difficulties arise. Specifically, even in the problem of the adsorption of a homogeneous polymer chain it is necessary to carry out some lengthy calculations, and these calculations do not yield reliable estimates of the critical indices. For example, the critical index φ [see (1)], which links the width of the adsorption transition with the length of the polymer, was calculated in Ref. 7 to within terms of second order in $\varepsilon = 4 - d$:

$$\varphi = \frac{1}{2} - \frac{1}{16}\varepsilon + \frac{1}{32\cdot 64}(64\pi^2 - 156)\varepsilon^2 + O(\varepsilon^3). \tag{41}$$

When we substitute $\varepsilon = 1$ and $\varphi = 0.65$ into (41), we find that the terms of second order in ε make a contribution roughly four times that of the terms of first order. Accordingly, it is more reliable to use the value[8] $\varphi = 0.59$ found by numerical simulation. The average number of adsorbed monomers at the adsorption point is

$$\mathcal{N} \sim N^{\varphi}. \tag{42}$$

Using the estimates of Sec. 2, we find the length scale of the polymer at which the inhomogeneity becomes important:

$$n_c \sim (\Delta w)^{-1/(\varphi - 1/2)}. \tag{43}$$

Comparing (42) and (41) with (2) and (4), we see that incorporating the three-dimensional interactions in a good solvent is equivalent to shifting the fractal dimensionality of the adsorbing surface by an amount $2\varphi - 1 \approx 0.18$. Since the chain at the adsorption point is definitely not a Gaussian chain because of the three-dimensional interactions, the length scale r_c is related to the length scale of the chain n_c, by

$$r_c \sim n_c^{\nu}, \tag{44}$$

where $\nu = 0.59$ (Ref. 9) is the index of the correlation length of a polymer in a good solvent.[5)]

Adsorption in a θ-solvent. In this case the second term on the right side of (40) dominates the three-dimensional interactions. That term describes the extent to which a monomer of species 1 or 2 is attracted or repelled, on the average, by all other monomers in the chain. The last term in (40) is inconsequential.

There can be two different situations: a) The monomers which are attracted to the adsorbing surface are, on the average, attracted to all other monomers in the chain. b) The monomers which are attracted to the surface are repelled by the monomers of the chain, and vice versa.

If the chain consists of monomers of many species, there is no single-valued relationship between the interaction with the surface and its interaction with the other monomers, but it can be described by a correlation coefficient $-1 \leqslant a \leqslant 1$, where the values $a = \pm 1$ correspond to cases a) and b).

In general, the complete renormalization-group equations consist of five equations for five different charges: the charges which describe the dispersion in the adsorption energy and the three-dimensional interaction, the ternary three-dimensional interaction, and the binary interaction on the adsorbing surface. The fifth charge describes the correlation between the sign of the interacting monomer (or segment of a chain) with a surface and the sign of its three-dimensional interaction with other monomers. We will derive and analyze the equations in a following paper; we content ourselves here with some qualitative remarks which are based on those equations.

1) There always exists a critical length scale at which the different sequences begin to differ greatly in terms of their macroscopic adsorption picture, although this scale may be very large if the seed constants satisfy certain relations.

2) If purely three-dimensional effects lead to an increase in the dispersion of the three-dimensional interaction over some length scale,[4] it will necessarily also induce an increase in the dispersion of the adsorption interaction.

3) If the dispersion of the three-dimensional interaction at the scales studied remains small, then for the adsorption of a macromolecule in case a) the critical adsorption scale will be smaller than in case b).

[1)] Gorsberg and Shchakhnovits[5] have studied the adsorption of a heteropolymer chain on a point and on a line in detail.

[2)] A dispersion in bond lengths can be incorporated quite easily, but it has no important consequences at large values of N.

[3)] Strictly speaking, this assertion is correct only in those lattice models (e.g., that of a square lattice rotated through 45°) in which two monomers which are adjacent along the chain can be on the adsorbing wall simultaneously. Nevertheless, it is possible to reduce the problem of adsorption on a wall to the problem with a permeable plane for any model. The difference in adsorption energies may differ from $kT \ln 2$.

[4)] The values given in parentheses correspond to a homogeneous polymer chain.

[5)] The coincidence of the numerical values of the indices φ and ν in the case $d = 3$ appears to be simply fortuitous.

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