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and Space Administration

Scientific and Technical
Information Branch

Summary

The adhesion between a polymer film and a metal surface is of great technological interest, with applications including space-based traction drives, human prostheses, and the production of integrated circuits. However, the prediction of adhesion and wear properties of polymer-coated metals is quite difficult because a fundamental understanding of the polymer-surface interaction does not yet exist.

A computer model for the conformation of a polymer molecule weakly adsorbed on a surface is discussed in this report. The chain conformation is assumed to be described by a partially directed non-self-avoiding random walk on a three-dimensional simple cubic lattice. An attractive surface potential is incorporated into the model through the use of a random-walk step-probability distribution that is anisotropic in the direction normal to the attractive surface. The surface potential is attractive over a range of a few lattice constants near the surface and infinitely repulsive as the distance from the surface approaches zero. The effects of variations in potential characteristics are qualitatively included by varying both the degree of anisotropy of the step distribution and the range of the potential.

Polymer conformation is characterized by the average chain end-to-end distance, average radius of gyration, and by the number of chain segments in contact with the surface. The scaling behavior of these quantities is investigated, and the fractal dimension is computed for models incorporating different attractive potentials.

The end-to-end distance, radius of gyration, and fractal dimension do not depend strongly on potential characteristics. The number of segments adsorbed, however, does depend on the potential characteristics; the number adsorbed increases with increasing potential range and with increasing anisotropy in the step distribution (corresponding to increasing potential strength). Since the strength of adhesion of the polymer to the surface depends in part on the fraction in contact with the surface, this result may have important consequences with regard to the friction and wear properties of polymer-metal interfaces.

Introduction

The nature of the adhesive forces between surfaces is of extreme importance in determining the friction and wear characteristics of the surfaces. Adhesion between metals has been used by Bowden and Tabor to partially explain such wear processes (refs. 1 and 2), and there have been a number of attempts to understand in more detail the nature of the adhesive forces. However, there have been few model calculations because of theoretical difficulties in treating surfaces and interfaces. To date, electron density functional theory (ref. 3) has been used by Lang and Kohn (ref. 4) to calculate surface energies of simple metals. Ferrante and Smith (refs. 5 and 6) have investigated the adhesion of similar and dissimilar metals in contact, and Rose, Ferrante, and Smith (ref. 7) have also discovered scaling laws which relate a wide range of experimental results to a universal adhesive-energy curve.

The theoretical treatment of the adhesion of a polymer to a metal surface presents greater difficulties than does metal-to-metal adhesion. Many polymers maintain their molecular identities even when adsorbed on an attractive surface. The electronic states in such chain molecules are very different from the delocalized states characteristic of metals. Since the polymer molecule has many internal degrees of freedom, the conformation of the molecule, as well as the binding of individual atoms to the surface, must be considered.

It is appropriate to begin a study of the polymer-surface interaction by considering the bonding of a single chain to an adsorbing surface. The problem divides naturally into two parts. The mechanism by which a single atom within the polymer chain bonds to the surface is of primary interest. Equally important, however, is the chain conformation, since it plays an important role in determining the fraction of monomers which are available for bonding. In general, the two parts of the problem are coupled; if the attractive surface potential is strong, the chain conformation may be greatly distorted, and the problem becomes virtually intractable. In the limit of weak adsorption, however, it may be assumed that the chain maintains its molecular character, so that chain conformation is still a meaningful method of characterizing the polymer.

The study of the conformation of a polymer chain in the vicinity of an attractive surface has been undertaken by a number of authors (refs. 8 to 33) using a variety of theoretical techniques. An assumption common to most of this work is that the polymer conformation may be approximated by a random walk on a lattice or tree structure of some sort. Many of the properties of simple random walks are well-known (refs. 34 and 35); thus the conformational statistics of such models are easily obtained. A simple random-walk model is not particularly realistic, however, in that it does not include the effect of excluded volume (i.e., the steric repulsion that prevents two atoms within the chain from coming arbitrarily close to one another) or the effect of the attractive surface potential. The excluded volume effect can be taken into account by incorporating self-avoidance into the random walk. Such a self-avoiding walk (SAW) model has not been solved exactly; thus researchers in the field have resorted to Monte Carlo calculations (refs. 25, 26, and 36), exact enumeration methods (refs. 24, 27, and 31), or renormalization group techniques (ref. 33) to investigate conformational statistics of both self-avoiding and non-self-avoiding walks. At present, exact enumeration methods are computationally practical for walks of approximately ten steps (ref. 27), so that the scaling behavior of these models must be investigated as well.

In this report, a computer model for the conformation of a polymer molecule weakly adsorbed on a surface is discussed. The chain conformation is assumed to be described by a partially directed non-self-avoiding random walk on a three-dimensional simple cubic lattice. The effects of an attractive surface potential are incorporated into the model through the use of a random-walk step-probability distribution that is anisotropic in the direction normal to the attractive surface. The surface potential is attractive over a range of a few lattice constants near the surface and infinitely repulsive as the distance from the surface approaches zero. The effects of variations in potential characteristics are included qualitatively by varying both the degree of anisotropy of the step distribution and the range of the potential. Excluded volume effects are ignored, but the aim here is primarily to obtain qualitative results that point the way for future work.

Polymer conformation is characterized by the average chain end-to-end distance and average radius of gyration (following Flory (ref. 36)) and by the number of chain segments in contact with the surface. The scaling behavior of these quantities is investigated (following deGennes (ref. 37)), and the fractal dimension (ref. 38) is computed for models incorporating different attractive potentials.

The end-to-end distance, radius of gyration, and fractal dimension do not depend strongly on potential characteristics. The number of segments adsorbed, however, does depend on the potential characteristics; the number adsorbed increases with increasing potential range and with increasing anisotropy in the step distribution (corresponding to increasing potential strength). Since the strength of adhesion of the polymer to the surface depends in part on the fraction in contact with the surface, this result may have important consequences with regard to the friction and wear properties of polymer-metal interfaces.

Survey of Previous Work

Experimental work on polymer adsorption has been reviewed by Silberberg (refs. 15 and 16), who lists a number of established facts:

(1) The amount of polymer adsorbed per unit area increases very rapidly with polymer concentration in solution and saturates at higher concentrations.

(2) The amount adsorbed depends on molecular weight; it increases with increasing molecular weight at small molecular weights and reaches saturation at higher molecular weights.

(3) A polymer chain adsorbs with a large fraction of its segments in contact with the adsorbing surface. This fraction, of the order of 0.5, is independent of polymer concentration in solution and independent of the fraction of the surface covered by the adsorbed polymer. It is also independent of solvent characteristics and of the adsorption characteristics of the surface.

(4) The adsorbed polymer consists of an alternating sequence of segments entirely adsorbed on the surface ("trains") and segments projecting entirely off the surface ("loops"). These loops are relatively short, and the adsorbed layer is often only 30 to 50 Å thick.

(5) The amount of polymer adsorbed is greatest when a poor solvent is used. The amount adsorbed decreases with increasing solvent power.

(6) The adsorbed polymer is often impossible to remove by washing with the solvent in which it had previously been dissolved, even if the solvent is pure. Often the polymer can be removed by washing with a more powerful solvent.

(7) Equilibrium requires a long time to occur, presumably because of the large size of the adsorbing molecules.

(8) The temperature dependence of the adsorption is weak, which indicates that only moderate adsorption energies are involved. This fact is consistent with the

assumption of weak adsorption discussed in item (4), but less consistent with item (6).

Previous theoretical work can be divided into two classes of approaches. In one approach, taken, for example, by Silberberg (refs. 15 to 17), Rubin (refs. 21 to 23), Roe (ref. 28), Hoeve et al. (refs. 18 to 20), and others, the polymer is assumed to consist of alternating loops and trains. Assumptions are made concerning the distributions of loop and train sizes, and partition functions for individual loops and trains are computed by assuming that each segment adsorbed on the surface has a characteristic energy which is lower than that of a segment in the solvent. The partition function for the entire chain is obtained, from which thermodynamic properties are calculated. The most important common feature of these calculations is the prediction of a critical segment adsorption energy.

A second theoretical approach involves simulation of the polymer conformation as a random walk on a lattice or tree structure. The polymer is assumed to win a small adsorption energy every time the random walk intersects the surface plane. Such calculations were undertaken by Lax (refs. 24 and 27), DiMarzio and McCrackin (ref. 25), and McCrackin (ref. 26). These workers observed a critical adsorption energy as well. It should be noted, however, that this method neglects the potential characteristics of the surface, except through the choice of the segment adsorption energy. Clearly, if the surface is attractive, the walk should be somewhat directed in the vicinity of the surface (i.e., the walk should be more likely to proceed toward the surface than away from it).

Lattice Models

In traditional studies of polymer conformation, the positions of atoms along the chain backbone are given in terms of the relative coordinates shown in figure 1 (refs. 36 and 39). The coordinate set consists of bond vectors of length $\{l_i\}$, bond angles $\{\theta_i\}$, and torsional angles $\{\phi_i\}$. It is usually assumed that only torsional degrees of freedom exist and that the bond lengths and angles are fixed. This assumption is consistent with predictions based on semi-empirical quantum-mechanical calculations for many polymers (ref. 40 and private communications by B. J. Orchard and A. J. Hopfinger, Case Western Reserve University).

In keeping with the preliminary and qualitative nature of this report, however, the traditional conformational variables are not used. Instead a simple lattice model is used to obtain information about chain conformation in the vicinity of an adsorbing surface. Such a lattice model does not incorporate the chain geometry of a specific polymer, but is entirely adequate for these preliminary calculations. Similar lattice models are discussed by Flory (ref. 36).

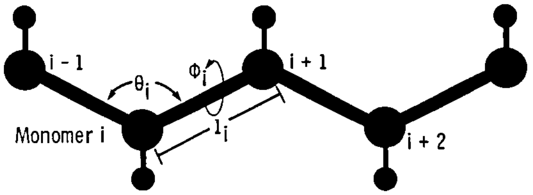

Figure 1.—Schematic of polymer conformation showing the conformational variables of bond angle (θ_i), bond length (l_i), and torsional angle (ϕ_i).

The lattice model considered in this report simulates polymer conformation by a random walk on a unit three-dimensional simple cubic lattice. For each lattice site visited (except the end sites), the walk also visits at least two nearest-neighbor sites, and thus establishes the linear-chain nature of the model. It is assumed that chain branching, bifurcation, and cross-linking do not take place. The model scheme is illustrated in figure 2. When considering such a lattice model, it must be realized that lattice points cannot represent individual monomers in a realistic way; the lack of flexibility of the bond angles means that adjacent monomers in most polymer chains cannot exist at nearest-neighbor points on a simple cubic lattice. This problem can be overcome, however, by assuming that a random-walk segment joining any two nearest-neighbor lattice points represents a chain segment which is small when compared with the whole chain, but contains enough monomers (and hence enough degrees of freedom) that successive segments are not geometrically prohibited from conforming to such a lattice.

In the Monte Carlo approach taken here, a "seed" monomer is planted on the lattice, and a chain consisting of many monomers is "grown" probabilistically from the seed monomer. In detail, a chain consists of $N-1$ segments connecting N lattice sites, with the ith lattice site located at $x_i = (x_i, y_i, z_i)$. The nearest-neighbor sites are given by

$$x_{NN} = x_i + \mathrm{d}x_j$$

where $\mathrm{d}x_j$ is one of the unit lattice vectors $\{(1,0,0), (-1,0,0), (0,1,0), (0,-1,0), (0,0,1), (0,0,-1)\}$.

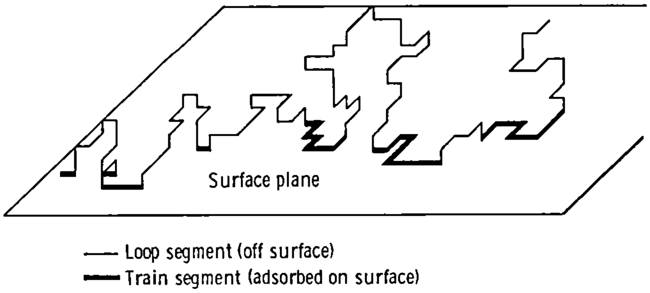

Figure 2.—Schematic of polymer conformation as simulated by a random walk on a unit three-dimensional simple cubic lattice.

The $i+1$ occupied site is chosen from among these nearest-neighbor sites according to the nearest-neighbor step-probability distribution

$$P[x_i, \mathrm{d}x_j]$$

which is the probability that, if the random walk has proceeded to site i, the next step is to the site located at

$$x_i + \mathrm{d}x_j$$

The step distribution is different for each of the models described in this section. In general, an attractive potential is associated with an adsorbing surface, a fact which is qualitatively included in the model through the use of a step distribution that is anisotropic in the direction normal to the surface for steps taken near the surface. The degree of anisotropy corresponds qualitatively to the strength of the potential; the stronger the potential, the more likely the random walk is to proceed toward the surface, and the less likely it is to proceed away from it. The range of the surface potential is varied by changing the distance from the surface over which the step distribution is anisotropic. The numeric values for the step distribution are chosen *a priori* to simulate various potential strengths and ranges; there is no detailed physical basis for these choices.

The adsorbing surface itself is assumed to be an exclusionary plane through which the random walk cannot pass. This assumption is consistent with a surface potential that is strongly repulsive at very short distances.

Three types of models were investigated:

(1) Free chain. This model is simply a three-dimensional random walk on a simple cubic lattice, with no step distribution anisotropy, simulating a chain in a solvent. The step distribution of this model is

$$P(x_i, \mathrm{d}x_j) = \frac{1}{6}$$

for all values of i and j. This model can in fact be solved analytically for chain end-to-end distance and radius of gyration and is included here for comparison with other models and for computer program verification.

(2) Free chain with exclusionary surface. This model is similar to model 1, except that the adsorbing surface is simulated by a plane at $z=0$ through which the random walk cannot pass. Any site lying in the $z=0$ plane is considered to be adsorbed. Thus for any site lying above the $z=0$ plane, conditions are the same as for the free chain model:

$$P(x_i, \mathrm{d}x_j) = \frac{1}{6}$$

For a site on the surface, however, the step distribution becomes

$$P(x_i, \mathrm{d}x_j) = 0 \qquad \mathrm{d}x_j = (0,0,-1)$$

$$= \frac{1}{5} \quad \text{otherwise}$$

(3) Free chain with attractive and repulsive surface. The interaction between the surface and a monomer within a polymer chain is not yet adequately known in detail; its general characteristics are, however, well-known. The interaction is attractive at distances of the order of interatomic spacings and repulsive at much smaller distances. The effects of such potentials are simulated by assuming that at large distances from the surface all step probabilities are 1/6, which is the free-chain value. At smaller distances, but still off the surface, the step distribution is taken to be a function of z only and to be isotropic in the direction parallel to the surface, so that

$$P(x_i, \mathrm{d}x_j) = \frac{1}{6} \qquad \mathrm{d}x_j = (\pm 1,0,0) \text{ or } (0,\pm 1,0)$$

The quantity $P(x_i, \mathrm{d}x_j)$ is anisotropic in z, so that

$$P[x_i, \mathrm{d}x_j = (0,0,-1)] > P[x_i, \mathrm{d}x_j = (0,0,1)]$$

For sites on the surface, the repulsive portion of the potential is simulated by an exclusionary plane, as in model 2.

Four types of attractive potentials were investigated:

(a) Narrow, deep. Free-chain behavior exists to within three lattice constants of the surface, and the step distributions are

$$P[x_i, \mathrm{d}x_j = (0,0,-1)] = \frac{8}{27} \qquad z_i < 3$$

$$P[x_i, \mathrm{d}x_j = (0,0,1)] = \frac{1}{27} \qquad z_i < 3$$

$$P[x_i, \mathrm{d}x_j] = \frac{1}{6} \qquad \text{otherwise}$$

(b) Broad, deep. Free-chain behavior exists to within eight lattice constants of the surface, and the step distributions are

$$P[x_i, \mathrm{d}x_j = (0,0,-1)] = \frac{8}{27} \qquad z_i < 8$$

$$P[x_i,\mathrm{d}x_j=(0,0,1)]=\frac{1}{27} \qquad z_i<8$$

$$P[x_i,\mathrm{d}x_j]=\frac{1}{6} \qquad \text{otherwise}$$

(c) Narrow, shallow. Free-chain behavior exists to within three lattice constants of the surface, and the step distributions are

$$P[x_i,\mathrm{d}x_j=(0,0,-1)]=\frac{2}{9} \qquad z_i<3$$

$$P[x_i,\mathrm{d}x_j=(0,0,1)]=\frac{1}{9} \qquad z_i<3$$

$$P[x_i,\mathrm{d}x_j]=\frac{1}{6} \qquad \text{otherwise}$$

(d) Broad, shallow. Free-chain behavior exists to within eight lattice constants of the surface, and the step distributions are

$$P[x_i,\mathrm{d}x_j=(0,0,-1)]=\frac{2}{9} \qquad z_i<8$$

$$P[x_i,\mathrm{d}x_j=(0,0,1)]=\frac{1}{9} \qquad z_i<8$$

$$P[x_i,\mathrm{d}x_j]=\frac{1}{6} \qquad \text{otherwise}$$

Characterization of Model Results

To characterize the computer-generated conformations, the average chain end-to-end distance R_E and the average radius of gyration R_G are selected as the relevant quantities, according to Flory (ref. 36). In addition, for models incorporating surfaces, the average number N_A of segments adsorbed is also computed. Chain lengths of 25 to 1000 sites are investigated, since these values are consistent with experimental data indicating that a typical polymer molecule contains of the order of 1000 to 10 000 monomers. Averages are taken over 1000 to 5000 chains, values which are sufficiently large to generate statistically repeatable data.

Another important parameter which characterizes polymer chain conformation is the Hausdorff-Besicovitch, or fractal, dimension (ref. 38). The fractal dimension (not necessarily an integer) of an object is a measure of the irregularity and fragmentation of the object and is a useful means of differentiating between relatively well-ordered objects (e.g., a crystalline polymer chain) and relatively disordered ones (such as the random chains considered in this report). Fractal dimensions have been calculated for a number of common objects, including coastlines, snowflakes, soot particles, Brownian paths, and, of primary interest here, simple random walks. The fractal dimension of such random walks can be easily obtained in two ways. Witten and Sander (ref. 41) showed (in the context of diffusion-limited aggregation of clusters) that the fractal dimension can be obtained from the density-density correlation function $C(r)$:

$$C(r)=[1/N]\langle \rho(r')\rho(r+r')\rangle$$

For r greater than a few lattice spacings but much smaller than the whole cluster, $C(r)$ is of the form $C(r)\sim r^{-\alpha}$. The fractal dimension D is given by $D=d-\alpha$, where d is the familiar Euclidean dimension of the cluster.

The fractal dimension can also be obtained by observing that the radius of gyration R_G also exhibits a power-law behavior, this time on the number of sites N in the cluster:

$$R_G \propto N^{\beta}$$

The fractal dimension D is given by $D=1/\beta$ (ref. 41). In this report, the second of these methods is used to determine D.

Results and Discussion

The results of a number of computer simulations of chain conformation are displayed in tables I to VIII and figures 3 to 5. Tables I to VI contain average values of chain end-to-end distance R_E, radius of gyration R_G, and number of segments adsorbed N_A (except table I). Each average is taken over M chains, with each chain incorporating N random-walk steps.

The distance R_E and the radius R_G exhibit similar behavior for the free-chain and free-chain-with-exclusionary-plane models. However, three of the four models incorporating attractive potentials show different

TABLE I.—FREE CHAIN

Number of random-walk steps, N	Number of chains per trial, M	End-to-end distance, R_E	Radius of gyration, R_G
25	5000	4.525	1.983
50	4000	6.486	2.804
100	2000	9.169	3.975
250	2000	14.698	6.308
500	1000	20.994	8.907
1000	1000	29.432	12.603

TABLE II.—FREE CHAIN WITH EXCLUSIONARY PLANE

Number of random-walk steps, N	Number of chains per trial, M	End-to-end distance, R_E	Radius of gyration, R_G	Number of segments adsorbed, N_A
25	5000	4.544	1.925	6.670
50	4000	6.501	2.702	9.749
100	2000	9.243	3.826	13.759
250	2000	14.727	6.046	21.526
500	1000	21.091	8.563	30.453
1000	1000	29.583	12.044	42.448

TABLE III.—FREE CHAIN WITH NARROW, DEEP POTENTIAL

Number of random-walk steps, N	Number of chains per trial, M	End-to-end distance, R_E	Radius of gyration, R_G	Number of segments adsorbed, N_A
25	5000	3.697	1.702	12.008
50	4000	5.265	2.357	22.719
100	2000	7.365	3.294	43.767
250	2000	11.858	5.229	105.89
500	1000	17.207	7.425	204.45
1000	1000	24.037	10.487	393.79

TABLE IV.—FREE CHAIN WITH BROAD, DEEP POTENTIAL

Number of random-walk steps, N	Number of chains per trial, M	End-to-end distance, R_E	Radius of gyration, R_G	Number of segments adsorbed, N_A
25	5000	3.671	1.696	12.039
50	4000	5.196	2.339	22.914
100	2000	7.222	3.250	44.358
250	2000	11.614	5.141	110.17
500	1000	16.605	7.209	220.60
1000	1000	23.102	10.164	438.60

TABLE V.—FREE CHAIN WITH NARROW, SHALLOW POTENTIAL

Number of random-walk steps, N	Number of chains per trial, M	End-to-end distance, R_E	Radius of gyration, R_G	Number of segments adsorbed, N_A
25	5000	4.102	1.816	8.993
50	4000	5.892	2.550	15.002
100	2000	8.407	3.615	25.228
250	2000	13.658	5.807	48.696
500	1000	19.772	8.289	79.638
1000	1000	28.061	11.779	123.35

TABLE VI.—FREE CHAIN WITH BROAD, SHALLOW POTENTIAL

Number of random-walk steps, N	Number of chains per trial, M	End-to-end distance, R_E	Radius of gyration, R_G	Number of segments adsorbed, N_A
25	5000	3.960	1.779	9.058
50	4000	5.501	2.462	15.626
100	2000	7.587	3.412	28.246
250	2000	12.019	5.328	65.190
500	1000	17.228	7.473	124.96
1000	1000	23.967	10.482	242.33

TABLE VII.—SCALING BEHAVIOR OF CHARACTERISTIC QUANTITIES

Model	Scaling exponents			Fractal dimension, D
	End-to-end distance, S_E	Radius of gyration, S_G	Number adsorbed, S_A	
Free chain	0.5086	0.5016	--------	1.994
Free chain with exclusionary plane	.5088	.4982	0.4992	2.007
Narrow, deep potential	.5098	.4949	.9491	2.021
Broad, deep potential	.5011	.4869	.9773	2.054
Narrow, shallow potential	.5228	.5086	.7143	1.966
Broad, shallow potential	.4907	.4804	.8591	2.081

TABLE VIII.—DATA SCATTER TEST

[1000-Step walks with 1000 chains per trial.]

Trial	End-to-end distance, R_E	Radius of gyration, R_G	Number of segments adsorbed, N_A
1	24.549	10.490	393.17
2	23.836	10.342	392.32
3	23.878	10.530	393.41
4	23.364	10.517	393.06

behavior. The narrow, deep; broad, deep; and broad, shallow potentials yield $R_E = 23$ to 24 and $R_G = 10$ for $N = 1000$, while the narrow, shallow potential yields $R_E = 28$ and $R_G = 12$, values similar to those for the free-chain model. While we neither look for, nor observe, a critical adsorption energy, the behavior of R_E for the most attractive potentials (and hence the ones that exhibit the largest N_A) is qualitatively similar to other work in that R_E attains its minimum value for such potentials. The number of segments adsorbed N_A, on the other hand, is more sensitive to potential characteristics than are R_E and R_G. The quantity $N_A(N = 1000)$ is calculated to be 394, 439, 123, and 242 for the narrow, deep; broad, deep; narrow, shallow; and broad, shallow potentials, respectively. This variation in the number adsorbed is expected to have important consequences with regard to the strength of the adhesive bond; since bonding energy per monomer is fixed, the total molecular bonding energy will depend on the number of monomers near enough to the surface that bonding can take place.

The scaling behavior (with N) of the various model parameters is shown in table VII. Each of the three parameters (R_E, R_G, and N_A) is assumed to exhibit power-law dependence on N, for example

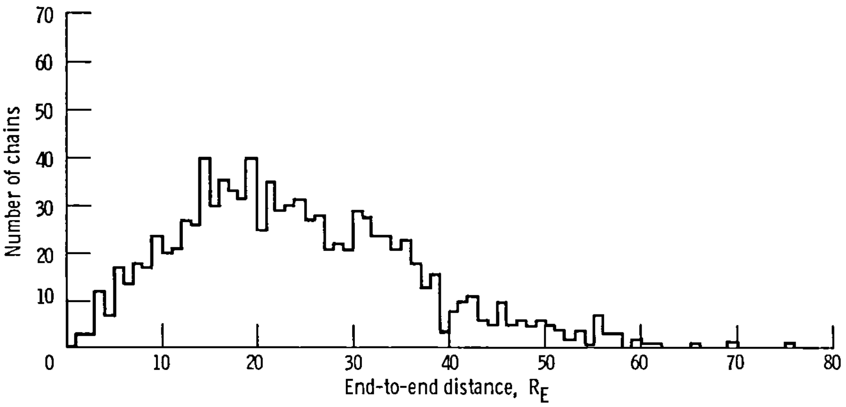

Figure 3.—Distribution of chain end-to-end distance in lattice constants.

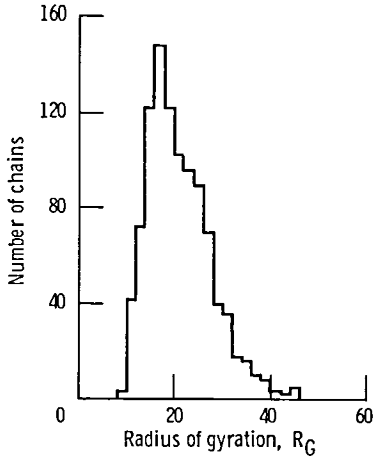

Figure 4.—Distribution of chain radius of gyration in lattice constants.

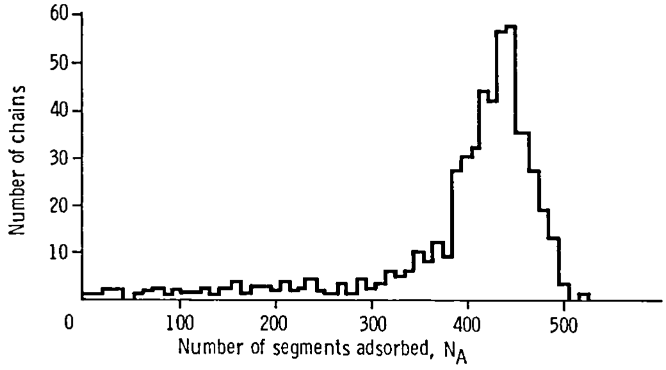

Figure 5.—Distribution of number of segments adsorbed.

$$R_E \propto N^{S_E}$$

The scaling exponent S_E is computed by performing a least-squares fit of $\ln R_E$ as a function of $\ln N$. The scaling exponents for R_G and N_A are computed in a similar manner. The fractal dimension D is the inverse of the R_G scaling exponent.

The scaling exponents and fractal dimension are shown for all models in table VII. Values of S_E and S_G are not strongly dependent on potential characteristics; S_E varies from 0.49 to 0.52, while S_G ranges from 0.48 to 0.51, with the fractal dimension in the range 1.99 to 2.08. The lack of variation in the fractal dimension indicates that each walk maintains its random nature, regardless of potential characteristics. It should be noted that the fractal dimension for the unconstrained free-chain model is 1.994, quite close to the value of 2 quoted by Mandelbrot (ref. 38) for Brownian random walks in Euclidean dimensions ≥ 2.

As previously stated, N_A is much more sensitive to potential characteristics, and this sensitivity is reflected in the scaling behavior. The scaling exponent S_A ranges from 0.50 (free chain with exclusionary plane) to 0.98 (broad, deep potential). There is little difference between the broad, deep and narrow, deep exponents; the potential is sufficiently attractive that its range is not a significant factor. On the other hand, the narrow, shallow exponent is somewhat different from the broad, shallow one; the potential is weak enough that the range is important. It should be noted that other workers (summarized in ref. 24) found S_A to have the value 0.5 at the critical adsorption energy. Their work, as previously noted, neglects the coupling of potential characteristics to the random walks; therefore their models are similar to the free-chain-with-exclusionary-plane model of this report. Thus the scaling exponent value $S_A = 0.4992$ agrees with earlier theoretical work. Also, this report is in qualitative agreement with earlier theoretical and experimental work in that chains are found to consist of sequences of short loops and adsorbed trains.

The values of N (chain size) and M (number of chains per trial) yield statistically reasonable results in terms of scatter about mean values of calculated parameters and in terms of repeatability. A typical set of histograms (for the narrow, deep potential with $M = 1000$ and $N = 1000$) is shown in figures 3 to 5.

To determine the repeatability of the results, four trials were performed. Each trial used a different value for the random number generator seed. The ranges of values of the various parameters are shown in table VIII. The results show that there is excellent agreement among the values obtained from the four trials.

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Cleveland, Ohio, January 29, 1985

References

1. Bowden, Frank Phillip; and Tabor, David: The Friction and Lubrication of Solids. Clarendon Press (London), 1950.
2. Tabor, D.: Interaction Between Surfaces: Adhesion and Friction. Surface Physics of Materials. Vol. 2, J. M. Blakely, ed., Academic Press, 1975, pp. 476-532.
3. Kohn, W.; and Sham, L. J.: Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. A, vol. 140, no. 4, Nov. 15, 1965, pp. 1133-1138.
4. Lang, N. D.; and Kohn, W.: Theory of Metal Surfaces: Charge Density and Surface Energy. Phys. Rev. B, vol. 1, no. 12, June 15, 1970, pp. 4555-4568.
5. Ferrante, John; and Smith, John R.: Theory of Metallic Adhesion. Phys. Rev. B, vol. 19, no. 8, Apr. 15, 1979, pp. 3911-3920.
6. Ferrante, John; and Smith, John R.: Bull. Am. Phys. Soc., vol. 26, 1981, pp. 428.
7. Rose, J. H.; Ferrante, John; and Smith, John R.: Universal Binding Energy Curves for Metals and Bimetallic Interfaces. Phys. Rev. Lett., vol. 47, no. 9, Aug. 31, 1981, pp. 675-678.
8. Frisch, H. L.; Simha, Robert; and Eirich, F. R.: Statistical Mechanics of Polymer Adsorption. J. Chem. Phys., vol. 21, no. 2, Feb. 1953, pp. 365-366.
9. Simha, Robert; Frisch, H. L.; and Eirich, F. R.: The Adsorption of Flexible Macromolecules. J. Phys. Chem., vol. 57, no. 6, June 1953, pp. 584-589.
10. Frisch, H. L.; and Simha, Robert: The Adsorption of Flexible Macromolecules. II. J. Phys. Chem., vol. 58, no. 6, June 1954, pp. 507-512.
11. Frisch, H. L.: Polymer Chain Configuration Near a Boundary Exerting Forces. J. Phys. Chem., vol. 59, no. 7, July 1955, pp. 633-636.
12. Frisch, H. L.; and Simha, Robert: Monolayers of Linear Macromolecules. J. Phys. Chem., vol. 24, no. 4, Apr. 1956, pp. 652-655.
13. Frisch, H. L.; and Simha, Robert: Statistical Mechanics of Flexible High Polymers at Surfaces. J. Chem. Phys., vol. 27, no. 3, Sept. 1957, pp. 702-706.
14. Higuchi, W. I.: Effects of Short Range Surface-Segment Forces on the Configuration of an Adsorbed Flexible Chain Polymer. J. Phys. Chem., vol. 65, no. 3, Mar. 1961, pp. 487-491.
15. Silberberg, A.: The Adsorption of Flexible Macromolecules. Part I. The Isolated Macromolecule at a Plane Interface. J. Phys. Chem., vol. 66, no. 10, Oct. 1962, pp. 1872-1883.
16. Silberberg, A.: The Adsorption of Flexible Macromolecules. Part II. The Shape of the Adsorbed Molecule; The Adsorption Isotherm, Surface Tension, and Pressure. J. Phys. Chem., vol. 66, no. 10, Oct. 1962, pp. 1884-1907.
17. Silberberg, A.: Adsorption of Flexible Macromolecules. III. Generalized Treatment of the Isolated Macromolecule; The Effect of Self-Exclusion. J. Chem. Phys., vol. 46, no. 3, Feb. 1, 1967, pp. 1105-1144.
18. Hoeve, C. A. J.: On the General Theory of Polymer Adsorption at a Surface. J. Polym. Sci. Part C, no. 30, 1970, pp. 361-367.
19. Hoeve, C. A. J.: Theory of Polymer Adsorption at Interfaces. J. Polym. Sci, Part C, no. 34, 1971, pp. 1-10.
20. Hoeve, C. A. J.; DiMarzio, E. A.; and Peyser, P.: Adsorption of Polymer Molecules at Low Surface Coverage. J. Chem. Phys., vol. 42, no. 7, Apr. 1, 1965, pp. 2558-2563.
21. Rubin, Robert J.: Random-Walk Model of Chain-Polymer Adsorption at a Surface. J. Chem. Phys., vol. 43, no. 7, Oct. 1, 1965, pp. 2392-2407.
22. Rubin, Robert J.: A Random Walk Model of Chain Polymer Adsorption at a Surface. 2. Effect of Correlation Between Neighboring Steps. J. Res. Natl. Bur. Stand. Sect. B, vol. 69, no. 4, 1965, pp. 301-312.
23. Rubin, Robert J.: A Random Walk Model of Chain Polymer Adsorption at a Surface. 3. Mean Square End-To-End Distance. J. Res. Natl. Bur. Stand. Sect. B, vol. 70, no. 4, 1966, pp. 237-247.
24. Lax, Melvin: Numerical Study of the Statistical Thermodynamic Properties of a Surface-Interacting Polymer Chain. J. Chem. Phys., vol. 61, no. 10, Nov. 15, 1974, pp. 4133-4137.
25. DiMarzio, Edward A.; and McCrackin, Frank L.: One-Dimensional Model of Polymer Adsorption. J. Chem. Phys., vol. 43, no. 2, July 15, 1965, pp. 539-547.
26. McCrackin, Frank L.: Configuration of Isolated Polymer Molecules Adsorbed on Solid Surfaces Studied by Monte-Carlo Computer Simulation. J. Chem. Phys., vol. 47, no. 6, Sept. 15, 1967, pp. 1980-1986.
27. Lax, Melvin: Configurational Properties of Self-Avoiding Walks Generated in the Presence of an Interacting Solid Barrier. J. Chem. Phys., vol. 60, no. 6, Mar. 15, 1974, pp. 2245-2249.
28. Roe, Ryong-Joon: Conformation of an Isolated Polymer Molecule at an Interface. II. Dependence on Molecular Weight. J. Chem. Phys., vol. 43, no. 5, Sept. 1, 1965, pp. 1591-1598.
29. Freed, K. F.: Excluded Volume Effects in Polymers Attached to Surfaces: Chain Conformational Renormalization Group. J. Chem. Phys., vol. 79, no. 6, Sept. 15, 1983, pp. 3121-3132.
30. Stanley, H. Eugene, et al.: Novel Superuniversal Behavior of a Random-Walk Model. Phys. Rev. Lett., vol. 51, no. 14, Oct. 3, 1983, pp. 1223-1226.
31. Ishanabe, Takao: Critical Exponents for Surface Interacting Self-Avoiding Lattice Walks. I. Three Dimensional Lattices. J. Chem. Phys., vol. 76, no. 11, June 1, 1982, pp. 5589-5594.
32. Ishanabe, Takao: Critical Exponents for Surface Interacting Self-Avoiding Lattice Walks. II. The Square Lattice. J. Chem. Phys., vol. 77, no. 6, Sept. 15, 1982, pp. 3171-3176.
33. Eisenriegler, E.; Kremer, K.; and Binder, K.: Adsorption of Polymer Chains at Surfaces: Scaling and Monte Carlo Analysis. J. Chem. Phys., vol. 77, no. 12, Dec. 15, 1982, pp. 6296-6320.
34. Montroll, E. W.: Random Walks on Lattices. Stochastic Processes in Mathematical Physics and Engineering, Richard Bellman, ed., Proceedings of Symposia in Applied Mathematics, Volume XVI, American Mathematical Society, 1964, pp. 193-220.
35. Barber, Michael N.; and Ninham, B. W.: Random and Restricted Walks. Gordon and Breach, 1970.
36. Flory, Paul J.: Statistical Mechanics of Chain Molecules. Interscience, 1969.
37. deGennes, Pierre-Gilles: Scaling Concepts in Polymer Physics. Cornell Univ. Press, 1979.
38. Mandelbrot, Benoit B.: Fractals: Form, Chance, and Dimension. W. H. Freeman, 1977.
39. Hopfinger, A. J.: Conformational Properties of Macromolecules. Academic Press, 1973.
40. Good, Brian Scott: Theory of Structure, Morphology, and Conductivity in Polymers. Ph.D. Thesis, Case Western Reserve Univ., 1983.
41. Witten, T. A., Jr.; and Sander, L. M.: Diffusion-Limited Aggregation, A Kinetic Critical Phenomenon. Phys. Rev. Lett., vol. 47, no. 19, Nov. 9, 1981, pp. 1400-1403.

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16. Abstract

The adhesion between a polymer film and a metal surface is of great technological interest, with applications including space-based traction drives, human prostheses, and the production of integrated circuits. However, the prediction of adhesion and wear properties of polymer-coated metals is quite difficult because a fundamental understanding of the polymer-surface interaction does not yet exist. A computer model for the conformation of a polymer molecule adsorbed on a surface is discussed in this report. The chain conformation is assumed to be described by a partially directed random walk on a three-dimensional simple cubic lattice. An attractive surface potential is incorporated into the model through the use of a random-walk step-probability distribution that is anisotropic in the direction normal to the attractive surface. The effects of variations in potential characteristics are qualitatively included by varying both the degree of anisotropy of the step distribution and the range of the anisotropy. Polymer conformation is characterized by the average end-to-end distance, average radius of gyration, and average number of chain segments adsorbed on the surface. In addition, the scaling behavior (with random-walk size) is investigated by computing the fractal dimension of each walk. The end-to-end distance, radius of gyration, and fractal dimension do not depend strongly on potential characteristics. The number of segments adsorbed, however, does depend on the potential characteristics; the fraction adsorbed increases with increasing potential range and with increasing anisotropy in the step distribution (corresponding to increasing potential strength). Since the strength of adhesion of the polymer to the surface depends in part on the fraction in contact with the surface, this result may have important consequences with regard to the friction and wear properties of polymer-metal interfaces.

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