I. INTRODUCTION

The interfacial properties of polymers and proteins at surfaces are important for many different industrial and biological processes including adsorption, adhesion, cohesion, wetting, chromatography, biomaterial compatibility, interactions with membranes, and molecular recognition. It is well known that the conformations of chain molecules are restricted in the presence of impenetrable surfaces, and that chains at interfaces can be considerably perturbed relative to their bulk conformations. One property of polymer molecules that has been studied only more recently, however, is the "internal structure" of a chain: certain periodic repeating patterns of intrachain contacts, specifically helices and parallel and antiparallel sheets. These conformations are commonly found in polymeric crystals and globular proteins. By exhaustive lattice simulations, it has been found that increasing the compactness of an isolated polymer chain molecule will lead to considerable internal structure. Thus the steric constraints imposed by compactness lead to a form of ordering. In this regard, this phenomenon bears some resemblance to the ordering that arises in lyotropic liquid crystals as the packing density increases. Since polymer chains near impenetrable surfaces are subject to steric constraints that restrict their conformations, we hypothesize that internal structure in polymers might be enhanced as they approach interfaces. We have recently found that such enhancement occurs for self-avoiding chains on two-dimensional square lattices near a one-dimensional line interface. However, because the nature of excluded volume can differ considerably in three dimensions relative to two dimensions, we have undertaken here a study of three-dimensional chains near a planar interface. Whereas we find that the total amount of internal structure is predicted to be smaller in three dimensions than in two dimensions, we find that the factor of increase in structure due to the presence of a surface is greater in three dimensions. We find different enhancements in three dimensions vs two dimensions of helices relative to sheets because of the different "dimensionalities" of these structures. Also we explore how increasing the chain–surface attraction leads to a transition from three to two dimensions; we find a single transition for chains in an inert solvent (0 intrachain attraction energy), but we find two transitions for chains in a very poor solvent (strong intrachain attraction energy).

II. THE MODEL

Details of exhaustive lattice simulation of isolated chains on three-dimensional simple cubic lattice have been explored.
presented elsewhere. Here we briefly review the main features of the method for isolated chains and describe the modification for incorporating the effects of a planar surf.

For a chain with \( n \) monomers, the \( i \)th monomer is represented by a unit cube centered at the lattice site \( r_i \), \( i = 1, 2, \ldots, n \). The bond length is normalized to unity. On the cubic lattice \( r_i = (k, l, m) \), where the integers \( k, l, m \) are coordinates relative to an arbitrary origin. Excluded volume is taken into account by forbidding more than one monomer to occupy the same lattice site, i.e., \( r_i \neq r_j \) for \( i \neq j \). All possible conformations of a single chain are enumerated. For each conformation, we compute the geometric centroid \( \mathbf{r}_{\text{cm.}} = \frac{1}{n} \sum_{i=1}^{n} \mathbf{r}_i \), which is equivalent to the center of mass (c.m.) if the monomers have identical masses, the square end-to-end distance \( R^e = \sum_{i=1}^{n-1} |\mathbf{r}_i - \mathbf{r}_{i+1}|^2 \), the square radius of gyration \( R^s = \frac{1}{n} \sum_{i=1}^{n} |\mathbf{r}_i - \mathbf{r}_{\text{cm.}}|^2 \), and the persistence length \( \xi = \frac{1}{2} \sum_{i=1}^{n-1} |\mathbf{r}_i - \mathbf{r}_{i+1}|^2 \). The number of topological contacts \( t \) of a conformation \(^2,4\) is the total number of monomer pairs \((ij)\) that are nearest neighbors in space, \(|r_j - r_i| = 1\), but are not nearest neighbors along the chain \( i \neq j - 1, j + 1 \). The maximum number of topological contacts possible \( t_{\text{max}} \) is a function of the chain length. \(^3,4\) Conformations with larger \( t \) are more compact. The number of monomers in various types of secondary structures are also computed (see Fig. 1).

A discussion of the physical basis for using cubic lattice configurations in Fig. 1 as models for common protein secondary structures can be found in Ref. 1. A useful tool in our analysis is the contact map,\(^2,4\) which is a simple two-dimensional representation of intrachain topological contacts. Any topological contact pair \((ij), i < j\), is represented by a dot at the \( i \)th row and \( j \)th column of the contact map. Secondary structures correspond to simple regular patterns on the contact map (Fig. 1).

The impenetrable surface is taken to be parallel to the \( x-y \) plane. For each conformation of a single chain, the minimum \( z \) coordinate \( z_{\text{min}} \) of the chain is identified in order to compute the shortest possible separation \( z_{\text{c.m.}} \) between the chain c.m. and a surface parallel to the \( x-y \) plane that the chain can approach along the direction of negative \( z \) axis without violating excluded volume (see Fig. 2(a)). Since there is a half-bond distance between the center of a monomer and its surface, \( z_{\text{c.m.}} = z - z_{\text{min}} + 1/2 \).

We first consider the problem when the distance \( z \) between the chain c.m. and the surface is minimum \( z = z_{\text{c.m.}} \), in which case there is at least one chain-surface contact. The number of chain-surface contacts \( s \) is then given by the number of monomers whose \( z \) coordinates are equal to \( z_{\text{min}} \), which is numerically equivalent to the total surface area of the conformation at \( z = z_{\text{min}} - 1/2 \). As an example, the conformation in Fig. 2(a) has \( s = 4 \), and monomers 40, 41, 42, and 43 are those that contact the surface when \( z = z_{\text{c.m.}} \). The maximum possible \( z_{\text{c.m.}} \) is one half the chain length, \( n/2 \), corresponding to the situation when the chain is linear and perpendicular to the surface, with a single chain-surface contact \( s = 1 \) between the surface and either end of the chain (see Fig. 2(bii)). On average, \( s \) increases with decreasing \( z_{\text{c.m.}} \); in the extreme situation when the chain conformation becomes two dimensional and lies flat on the surface, the distance between the chain c.m. and the surface is minimum \( z_{\text{c.m.}} = 1/2 \), while the number of chain-surface contacts is maximum \( s = n \). Lattice conformations related by rigid rotations and space inversion are considered to be distinguish-

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**FIG. 1.** Cubic lattice models of secondary structure and their contact maps. Dotted lines circumscribe the fundamental units in each secondary structure type that must be present for the configuration to qualify as the corresponding type of secondary structure (Ref. 4).
able in our exhaustive enumerations. However, for the present purpose, it is only necessary to generate conformations that are not related by rotations and inversions, since complete data for a class of conformations related by these transformations can be obtained simply by permuting the $\pm x$, $\pm y$, and $\pm z$ axes of any one of the conformations in the class. This reduces the size of any simulation to only about $1/48$ of all possible conformations.

To determine the variation of polymeric properties as the chains approach the surface, conformations are enumerated as a function of the chain-surface separation $z_{\text{cm}}$. The number of $n$-monomer conformations with $z_{\text{cm}} < z$ is denoted by $Q_a(n|z',z)$, where the subscript "a" specifies that the chain is "attached" or adhered to the surface, i.e., it has at least one chain-surface contact. This is in distinction to the superset of conformations, considered below, of "interfacial" (i) chains, those that are at or near an interface, including conformations that are not necessarily in contact with the surface. In the analysis below, conformations are grouped by $z_{\text{cm}}$ into distance intervals of $\delta z$ ($>0$). These distance intervals are labeled by $u$, with $z_u = u\delta z + 1/2$ and $u = 0, 1, 2, \ldots$. Here $Q_a$ represents the conformational freedom of attached chains as a function of the distance between the chain c.m. and the surface. Only conformational freedom and steric effects of excluded volume are taken into account in the enumeration of $Q_a$, so the quantity $Q_a(n|z')$ is independent of intrachain or chain-surface contact energy. The following are general properties: (i) The sum of all $Q_a$ is the number of all accessible conformations of an isolated chain $Q_0(n)$,

$$\sum_{u=0}^{\infty} Q_a(n|z_u,z_u+1) = Q_0(n); \quad (2.1)$$

(ii) Since the maximum possible $z_{\text{cm}}$ is $n/2$, $Q_a(n|z') = 0$ for $z' > z > n/2$. When conformations are grouped into distance intervals of width $\delta z$, $Q_a(n|z_u,z_u+1) = 0$ for $u > u_{\text{max}},$

where

$$u_{\text{max}} = \left\lfloor \frac{n-1}{2\delta z} \right\rfloor \quad (2.2)$$

and here $[x]$ is the greatest integer less than or equal to $x$ [this notation applies only to Eq. (2.2)]. (iii) Because any distance interval $z_0 < z_{\text{cm}} < z$ with $z_0 = 1/2$ as the lower bound contains the $z_{\text{cm}} = z_0 = 1/2$ planar conformations that configured on a square lattice, the inequality

$$Q_a(n|z_0,z) > Q_0(n) \quad (2.3)$$

holds for all $z > z_0$, where $Q_0(n)$ is the number of all accessible conformations on the two-dimensional square lattice. As an example, $Q_a(n|z_u,z_{u+1})$ for $n = 14$ and $\delta z = 1/8$ are given in Table I.

Next we consider "interfacial" chains, all chain conformations in the interfacial region with $n/2 > z > z_{\text{cm}}$, which may or may not have any chain-surface contacts ($z$ is the distance between the impenetrable planar surface and the c.m. of the chain). We adopt the definition [Fig. 2(b)] that a chain with $z < n/2$ is in the interfacial region, otherwise (for $z > n/2$) the chain is in the bulk. A chain molecule in the interfacial region is distinguished from a molecule in the bulk in that it is capable of making at least one chain-surface contact without altering the position of its center of mass. Thus attached chains constitute a subset of all interfacial chains.

The present model allows conformations to translate rigidly in steps of length $\delta z$ along the $z$ axis. Hence the number $Q_i(n|z_u,z_{u+1})$ of accessible $n$-monomer conformations, with or without chain-surface contacts, whose c.m. distance $z$ from the surface is within $z_u < z < z + \delta z = z_{u+1}$, is equal to the sum of all conformations with $z_{\text{cm}} < u$,

$$Q_i(n|z_u,z_{u+1}) = \sum_{v=0}^{u-1} Q_a(n|z_v,z_{v+1}) = Q_a(n|z_0,z_{u+1}). \quad (2.4)$$

This follows from the fact that each of the $Q_a(n|z_v,z_{v+1})$ conformations in all distance intervals $v < u$ can be translat-
TABLE I. \(Q_a(n|z_u, z_{u+1})\) is the number of attached conformations and \(Q_o(n|z_u, z_{u+1})\) is the number of interfacial conformations whose c.m. distance \(z\) is within interval \(u\), i.e., \(z_u < z < z_{u+1}\), where \(z_u = adz + 1/2\). The table provides exact enumeration data on three-dimensional simple cubic lattices for \(n = 14\) and \(\delta z = 1/8\). The number \(Q_a(n)\) of \(n\)-monomer two-dimensional square lattice conformations is 881 500 for \(n = 14\).

| \(u\) | \(Q_a(n|z_u, z_{u+1})\) | \(Q_o(n|z_u, z_{u+1})\) |
|------|------------------|------------------|
| 0    | 1 531 364        | 1 531 364        |
| 1    | 6 662 112        | 8 193 476        |
| 2    | 16 976 448       | 25 169 924       |
| 3    | 13 644 904       | 38 814 828       |
| 4    | 36 579 044       | 75 393 877       |
| 5    | 48 117 740       | 123 511 612      |
| 6    | 61 804 484       | 185 316 096      |
| 7    | 35 667 264       | 220 983 360      |
| 8    | 78 855 188       | 299 838 548      |
| 9    | 82 121 764       | 381 960 312      |
| 10   | 79 106 008       | 461 066 400      |
| 11   | 37 329 444       | 498 395 844      |
| 12   | 70 417 552       | 568 813 396      |
| 13   | 63 652 100       | 622 465 496      |
| 14   | 55 556 520       | 688 022 016      |
| 15   | 24 741 960       | 712 763 976      |
| 16   | 43 641 716       | 756 405 692      |
| 17   | 36 917 688       | 729 733 380      |
| 18   | 31 008 224       | 803 111 604      |
| 19   | 13 551 872       | 837 883 476      |
| 20   | 23 528 008       | 861 411 484      |
| 21   | 19 124 360       | 880 535 844      |
| 22   | 15 328 024       | 895 863 868      |
| 23   | 6 408 776        | 902 272 644      |
| 24   | 10 756 736       | 913 029 380      |
| 25   | 8 359 760        | 912 381 140      |
| 26   | 6 391 704        | 927 780 844      |
| 27   | 2 261 954        | 930 348 828      |
| 28   | 4 093 792        | 934 442 620      |
| 29   | 2 979 640        | 937 422 260      |
| 30   | 2 135 040        | 939 557 300      |
| 31   | 824 400          | 940 381 700      |
| 32   | 1 247 328        | 941 699 078      |
| 33   | 864 392          | 942 475 420      |
| 34   | 563 056          | 943 028 476      |
| 35   | 201 736          | 943 240 212      |
| 36   | 292 536          | 943 532 748      |
| 37   | 184 168          | 943 716 916      |
| 38   | 111 416          | 943 826 332      |
| 39   | 36 664           | 943 864 996      |
| 40   | 50 064           | 943 915 060      |
| 41   | 29 904           | 943 943 904      |
| 42   | 15 280           | 943 959 244      |
| 43   | 4 680            | 943 963 924      |
| 44   | 640              | 943 969 564      |
| 45   | 2 832            | 943 972 396      |
| 46   | 1 248            | 943 973 644      |
| 47   | 344              | 943 973 988      |
| 48   | 360              | 943 974 348      |
| 49   | 112              | 943 974 460      |
| 50   | 46               | 943 974 500      |
| 51   | 8                | 943 974 508      |
| 52   | 2                | 943 974 510      |
| 53   | 0                | 943 974 510      |

which is our main focus, although the definition of \(Q_a\) also applies to chains in the bulk. For chains in the bulk, i.e., for all distance intervals \(z > n/2\),

\[ Q_a(n|z_u, z_{u+1}) = Q_o(n|z_u, z_{u+1}) \quad (2.5) \]

As an example, \(Q_o(n|z_u, z_{u+1})\) tabulated in Table I and \(\delta z = 1/8\). The \(Q_o(n|z_u, z_{u+1})\) data in Table I indicate that as a chain approaches an impenetrable surface, conformational freedom diminishes. (The number of conformations decreases as the separation between chain c.m. and the impenetrable surface decreases.) Consequently, in the absence of contact interaction energies, there is an entropic contribution to the free energy that repels the chain from the surface. To bring the c.m. of interfacial chains from the \(\delta z\) neighborhood of \(z'\) to that of \(z\) requires the free energy

\[ \Delta G = -kT \ln \left( \frac{Q_o(n|z_u, z + \delta z)}{Q_o(n|z_u, z')} \right) \]

\[ = -kT \ln \left( \frac{Q_o(n|z_u, z' + \delta z)}{Q_o(n|z_u, z')} \right), \quad (2.6) \]

where \(k\) is the Boltzmann constant and \(T\) the absolute temperature. For \(z > n/2\), the denominators in the logarithms of the above equation become \(Q_o(n|z_u, z' + \delta z)\) and \(Q_o(n|z_u, z')\) are accessible in the first interval \(1/2 < z_u < 5/8\). The total number of conformations \(Q_o(n)\) in the bulk is 943 974 510, while the number of conformations \(Q_o(n|z_u, z_{u+1})\) accessible in the first interval \(1/2 < z_u < 5/8\) is 1 531 364 (Table I); hence by the above equation, the free energy is about 6.4\(kT\) to bring the chain c.m. from the bulk to the surface.

To simplify notation in our discussion below, we will abbreviate \(Q_o(n|z_u, z_{u+1})\) by \(Q_o(n|z_u)\) and \(Q_o(n|z_u, z_{u+1})\) by \(Q_o(n|z_u)\) when there is no danger of ambiguity. In adopting this simpler notation, it is understood that the distance interval width \(\delta z\) is included implicitly in \(Q_o(n|z_u)\) and \(Q_o(n|z_u, z_{u+1})\), and \(z\) can only take discrete values of \(z_u\) as labels of the distance intervals \(u = 0, 1, 2, \ldots\). The schematic notation \(\Sigma_z\) will be used to denote summation over all distance intervals in the interfacial region

\[ \Sigma_z \equiv \sum_{z_u}^{u/2} \Phi(z_u) \quad (2.7) \]

with \(\Phi(z_u)\) defined by Eq. (2.2). Unless otherwise stated, \(\delta z = 1/8\) is used in our analysis below and \(\Phi(z_u)\) is taken for \(u = 14\).
phenomena are predicted for terminally attached chains and their end-to-end distance of a chain increase when the chain c.m. approaches to within about twice the chain's average radius of gyration in the bulk. \cite{footnote1}

The mean-square radius of gyration $R_g^2$ for Z-P CO, $n = 14$ cubic lattice chains in the bulk is 1.93.\cite{footnote1} The presence of the surface affects the ensemble of interfacial conformations as outlined in Sec. II. Though all conformations in the interfacial region are affected by the surface, the results in Figs. 3(a), 3(b), and 3(c) indicate that the surface has nonnegligible effects on the average chain dimensions only when the chain c.m. approaches to within about twice the chain's average radius of gyration in the bulk.\cite{footnote1} The persistence length $\alpha$ \cite{footnote1} exhibits similar dependence on $z$ as $R_g^2$ and $R_\perp^2$. These features arise because chain molecules near, but not on, the surface are more compact than those in the bulk (see below). These results are obtained by computing the average properties at each $z$ using ensembles of $Q(nz)$ conformations as outlined in Sec. II. Though all conformations in the interfacial region are affected by the surface, the results in Figs. 3(a), 3(b), and 3(c) indicate that the surface has nonnegligible effects on the average chain dimensions only when the chain c.m. approaches to within about twice the chain's average radius of gyration in the bulk.\cite{footnote1} The root-mean-square radius of gyration $\sqrt{\langle R_g^2 \rangle} = \sqrt{\langle R_\perp^2 \rangle (n/\infty)}$, for $z \to \infty$, $n = 14$ cubic lattice chains in the bulk is 1.93.\cite{footnote1} This confirms observations from three-dimensional off-lattice Monte Carlo simulations.\cite{footnote1} The same "effective range" of surface influence also applies to two-dimensional chains near a one-dimensional wall.\cite{footnote1} The mean square radius and end-to-end distance of a chain increase when the chain c.m. is very close to the surface [Figs. 3(a) and 3(b)]. Similar phenomena are predicted for terminally attached chains (not considered here) by Douglas et al. using a continuum path-integral model.\cite{footnote1,footnote11} These effects may be attributed to the increased restriction on chain conformational freedom by excluded volume in a space near the impenetrable wall, which is of an effectively lower spatial dimension than that available to chains in the bulk.\cite{footnote10}

The ensemble of polymer conformations can be divided into subsets, each of which characterizes all the conformations with a given number $s$ of chain surface contacts. Not surprisingly, with increasing $s$, the conformational ensemble becomes increasingly "flattened" onto the surface [Figs. 3(a), 3(b), and 3(c)]. Note that averages in the first $z$ interval are close but not identical to the $s = n$ averages because the first $z$ interval ($1/2 < z < 5/8$) contains nonplanar conformations as well as planar conformations. When a chain molecule is constrained to make exactly one chain–surface contact ($s = 1$), lattice geometry dictates that the contact has to be made between the surface and one of the two chain ends, and the chain has to adopt a relatively extended conformation perpendicular to the surface to avoid additional chain–surface contacts. Hence the persistence length exhibits a sharp peak at $s = 1$ [Fig. 3(c)] and the perpendicular dimensions in Figs. 3(a) and 3(b) also peak at $s = 1$. The presence of the surface affects the ensemble of conformations in the interfacial region, for every c.m. position $z < n/2$, some conformations are eliminated because they run into the surface. As shown in Figs. 3(a) and 3(b), even the ensemble of interfacial $s = 0$ conformations are slightly distorted from that in the bulk; on the average, inter-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{(a) Mean square radius of gyration $R_g^2$. (b) Mean square end-to-end length $R_e^2$. As in (a), $\parallel$ and $\perp$ refer to the parallel and perpendicular components, respectively. The two dashed curves show the parallel and perpendicular components of average $R_e^2$ as functions of $s$. (c) Persistence length. (d) Number of topological and chain–surface contacts averaged over interfacial conformations $(t(nz))$, and $(s(nz))$, are shown as solid curves. The corresponding averages over attached conformations $(t(nz))_0$ and $(s(nz))_0$ are shown as dashed curves.}
\end{figure}
facial chains are slightly flattened along the direction perpendicular to the surface.

Figure 3(d) shows the average number of intrachain topological contacts \( t \) and the average number of chain–surface contacts \( s \) among interfacial conformations. Averages over two different ensembles are given: (i) all interfacial conformations (attached chains included) with or without surface contacts; and (ii) all attached chains with at least one surface contact. To evaluate these averages as functions of \( z \), we define \( Q_i(n|z;t,s) \) and \( Q_a(n|z;t,s) \), respectively, as the number of interfacial and attached conformations at \( z \) from the surface with \( t \) topological contacts and \( s \) chain–surface contacts. By definition,

\[
\sum_{t=0}^{t_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} Q_i(n|z;t,s) = Q_i(n|z),
\]

\[
\sum_{t=0}^{t_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} Q_a(n|z;t,s) = Q_a(n|z),
\]

(3.1)

and \( Q_i(n|z;0,0) = 0 \). Since the number of \( z = 0 \) conformations at \( z \) is the difference between the number of all accessible chains and the number of attached chains,

\[
Q_i(n|z;t,s) = \left\{ \begin{array}{ll}
\sum_{t=0}^{t_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} [Q_i(n|z;t,s) - Q_a(n|z;t,s)], & \text{for } s = 0 \\
Q_a(n|z;t,s), & \text{for } s > 0,
\end{array} \right.
\]

(3.2)

where the terms in the first summation (enclosed by square brackets) equal \( Q_i(n|z - \delta z;t,s) \). In this notation, the average of any function \( u(n|z;t,s) \) of \( t \) and \( s \) over the ensemble of interfacial (i) or attached (a) \( n \)-monomer conformations at \( z \) is given by

\[
\langle u(n|z) \rangle_{i/a} = \sum_{t=0}^{t_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} u(n|z;t,s) Q_{i/a}(n|z;0) / \sum_{t=0}^{t_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} Q_{i/a}(n|z;0),
\]

(3.3)

where the subscript “i/a” in \( Q_{i/a} \) is a shorthand for \( Q_i \) or \( Q_a \). Substituting Eq. (3.2) into Eq. (3.3), we obtain the interfacial average of \( t \) and \( s \) over

\[
\langle t(n|z) \rangle_i = \sum_{t=0}^{t_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} t Q_i(n|z;t,s) / \sum_{t=0}^{t_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} Q_i(n|z;t,s)
\]

(3.4)

and

\[
\langle s(n|z) \rangle_i = \sum_{t=0}^{t_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} s Q_i(n|z;t,s) / \sum_{t=0}^{t_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} Q_i(n|z;t,s)
\]

(3.5)

as functions of \( z \).

Figure 3(d) shows that the average number of intrachain contacts \( \langle t(n|z) \rangle \), and the average number of chain–surface contacts \( \langle s(n|z) \rangle \), are influenced by the surface within the same effective range of approximately \( 2\sqrt{(R_{\text{c.m.}}/z)} \) as are the other conformational properties shown in Figs. 3(a)–3(c). There are essentially no surface contacts for \( z > 2\sqrt{(R_{\text{c.m.}}/z)} \), and the average number of intrachain topological contacts levels off at approximately the same \( z \). The average number of chain–surface contacts increases sharply as the chain approaches the surface, limiting to the maximum value \( n \) as \( z \to 1/2 \). The average number of topological contacts \( \langle t(n|z) \rangle \), in Fig. 3(d) peaks around \( z = 1 \), indicating that compact three-dimensional chains are favored near a two-dimensional surface. However, \( \langle t(n|z) \rangle \), diminishes when the chain moves further towards the surface, simply because flattened conformations very near the surface do not allow the formation of maximum number of topological contacts as in the bulk. For example, for the \( n = 14 \) chains shown in Fig. 3(d), no maximally compact \( t = t_{\text{max}} \) chains can configure with \( z < 7/18 \). Similar features were also observed for two-dimensional chains near a linear surface.

When the c.m. position is increased beyond about \( z = 1 \), the rate of decrease of the average number of intrachain topological contacts \( \langle t(n|z) \rangle \) for attached chains is much greater than those for all interfacial chains. This is because each attached chain is constrained to have at least one surface contact, therefore all attached chains with large c.m. distance \( z \) from the surface must be quite extended and thus cannot form many intrachain topological contacts. For the same reason, the average number of chain–surface contacts \( \langle s(n|z) \rangle \) for attached chains approaches unity as \( z \) approaches the boundary between the interfacial and bulk region at \( z = n/2 \).

We now consider the probabilities of intrachain contacts. The main question addressed in this section is how the likelihood of a contact between monomers (ij) is affected by the proximity of a chain to a surface. First, consider chains in the absence of a surface (i.e., in the bulk). Compactness is defined\(^{3,4} \) as the ratio \( \rho = t/t_{\text{max}} \) between the number \( t \) of intrachain topological contacts and the maximum number \( t_{\text{max}} \) of contacts possible for that chain length. We denote the number of all accessible \( n \)-monomer conformations by \( Q_0(n) \), the number of conformations with a total of \( t \) contacts by \( Q^{(t)}(n) \), and the number of conformations with a total of \( t \) contacts that include a specific contact between monomer i and j by \( Q^{(t)}(n;ij) \). Then \( \Delta G = -kT \ln \left[ Q^{(t)}(n;ij)/Q_0(n) \right] \) is the entropic free energy of the ensemble of chain conformations with a specific number \( t \) of topological contacts, relative to the ensemble of all accessible conformations in the bulk. A few of these free energy differences are plotted as horizontal dashed lines in Fig. 4(c); for instance, there is an entropic free energy increase of approximately \( 9kT \) when \( n = 14 \) chains collapse from the full ensemble to maximum compactness.

The relative probabilities of all possible intrachain contacts in ensembles of fixed \( t \) are shown in Figs. 4(a) and 4(b). These single-contact topological free energy surfaces\(^{2-4} \) are constructed by plotting the contours of the quantity \( -kT \ln \{ Q^{(t)}(n;ij)/Q_0(n) \} + \text{constant} \) at the (ij) position of the contact map. The \( t = 3 \) plot [Fig. 4(a)] has features very similar to that of the full ensemble (i.e., all \( t \), 0 \( \leq t \leq t_{\text{max}} \)) shown in Fig. 5 of Ref. 4, the difference in free energy between the most disfavored contact at (2,13) and the most favored contacts at (1,4) and (11,14) is about 2.9\( kT \). By contrast, the \( t = 8 \) plot [Fig. 4(b)] shows an essentially flat landscape, the difference in free energy between the most disfavored and the most favored contact is only 0.6\( kT \). This confirms earlier observations in both two\(^3 \) and three\(^4 \) dimensions that contact formation becomes nearly
is very near the surface. At distance interval \( u = 0 \) proach that for a two-dimensional chain when the chain c.m. cal free energy surfaces in Figs. 5(a) and 5(b) show that group interfacial conformations into ensembles of specific \( z \) of the chain from the surface? Now we

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**FIG. 4.** Effects of chain compactness on contact formation, \( n = 14 \). Single-contact topological free energy surface in the ensemble of conformations with (a) \( t = 3 \) and (b) \( t = 8 \) topological contacts. Contours are given in 0.3\( kT \) steps. The number of \( n = 14 \) conformations with specific \( t \) can be found in Table III of Ref. 4. (c) Dashed horizontal lines mark the entropic free energy levels, relative to the full ensemble, for ensembles of conformations with specific \( t \). Solid curves show the variation with contact order \( k \) of average entropic free energy per contact for \( t = 1, 3, 8, \) and 10. The solid curve with squares shows the corresponding variation for the full ensemble (all \( t \)).

“ideal” in compact chains; i.e., it becomes nearly independent of \( i \) and \( j \). This feature is further illustrated by the solid curves in Fig. 4(c), which give the average entropic free energy per contact as functions of the contact order \( k \) (i.e., distance intervals of \( z \)) instead of grouping conformations with \( t \) contacts, the average entropic free energy \( \Delta G \) per contact of order \( k \), relative to that of the full ensemble, is defined as

\[
kT \ln Q_0(n) - kT \ln \left[ \frac{\sum_{i-j=k} Q^{(t)}(n;ij)P(ij)}{\sum_{i-j=k} P(ij)} \right],
\]

(3.6)

where \( P(ij) \) is the probability of the contact \( (ij) \) in the ensemble. Since \( P(ij) = Q^{(t)}(n;ij)/Q^{(t)}(n) \), the above quantity reduces to

\[
kT \ln Q_0(n) - kT \ln \left[ \frac{\sum_{i-j=k} Q^{(t)}(n;ij)^2}{\sum_{i-j=k} Q^{(t)}(n;ij)} \right].
\]

(3.7)

The corresponding definition of average entropic free energy \( \Delta G \) per contact of order \( k \) for the full ensemble is obtained by replacing \( Q^{(t)}(n;ij) \) by \( Q(n;ij) = \sum_{t=0}^{t_{\text{max}}} Q^{(t)}(n;ij) \) in Eq. (3.7). Figure 4(c) shows the variation of the \( k \) dependence of these average free energies with the \( t \) value of the ensembles. For conformations in the full ensemble (solid curve with squares in Fig. 4(c)), contacts of lower orders are favored, since the average free energy first increases with \( k \) and peaks at \( k = 11 \) for \( n = 14 \). However, as \( t \) increases to \( t_{\text{max}} \), the corresponding curve is essentially level, implying that contacts of all orders are approximately equally probable.

How does the probability of a contact \( (ij) \) depend on the c.m. distance \( z \) of the chain from the surface? Now we group interfacial conformations into ensembles of specific \( z \) (i.e., distance intervals of \( z \)) instead of grouping conformations according to \( t \). Results are given in Fig. 5. The topological free energy surfaces in Figs. 5(a) and 5(b) show that relative formation probabilities of different contacts approach that for a two-dimensional chain when the chain c.m. is very near the surface. At distance interval \( u = 0 \) (1/2\( z < 5/8 \)), the free energy surface of Fig. 5(a) has features similar to that of two-dimensional square lattice chains (Fig. 6 of Ref. 2). For instance, for \( n = 14 \), the most disfavored contact is (3,12) for both the \( u = 0 \) interfacial chains and two-dimensional chains. The difference in entropic free energy between the most disfavored contact (3,12) and the most favored contacts at (1,4) and (11,14) is 2.83\( kT \) for \( u = 0 \) (three-dimensional) interfacial chains and 3.17\( kT \) for two-dimensional chains. When the chain c.m. is only less than one half-bond length further from the surface, the free energy surface approaches that for three-dimensional chains in the bulk. In Fig. 5(b), at distance interval \( u = 3 \) (7/8\( z < 1 \)), the most disfavored contact among interfacial chains is shifted to (2,13), the same contact that is most disfavored in the bulk (Fig. 5 of Ref. 4). The entropic free energy difference between the most disfavored and the most favored contact is 2.42\( kT \) for interfacial chains at distance interval \( u = 3 \) compared to 2.59\( kT \) in the bulk. Figure 5(c) shows the average entropic free energy per contact for contacts of different orders \( k \) (solid curves). In the open ensemble, loops of small \( k = |i-j| \) are favored relative to larger loops. Increasing the compactness in bulk chains increases the probabilities of larger loops more than it increases the probabilities of smaller loops. In contrast, the proximity of a surface does not change much the relative probabilities of larger vs smaller loops. The \( k \) dependence changes gradually from that of a three-dimensional chain in the bulk to that of a two-dimensional chain (otherwise unconstrained). The solid curves share similar profiles, though low-order contacts are slightly more favored relative to high-order contacts in two-dimensional chains as compared to three-dimensional chains.\(^4\) The dashed horizontal lines in Fig. 5(c) mark the entropic free energy levels of interfacial chains as a function of \( z \). Entropic free energy does not increase sharply until the chain c.m. is well within the effective range of influence \( \gamma \sqrt{\left( R \over 2 \right)} \) of the surface. For \( n = 14 \), only 1.15\( kT \) is required to bring the chain c.m. from the bulk to within one bond length (\( u = 8 \)) of closest approach to the surface, while
6.98kT is required to completely flatten the chain onto the surface. Figure 6 shows that surfaces tend to favor the formation of certain classes of contacts in polymers—specifically, they favor those contacts that correspond to helix and antiparallel sheet conformations. Three topological free energy surfaces for interfacial chains at distance interval $u = 1$ ($5/8 < z < 3/4$) are shown in Fig. 6. The contour plots give the relative free energies (negative logarithm of relative formation probabilities) of all possible second contacts after a given first contact has already been formed; see Ref. 4. The three plots in Fig. 6 indicate that secondary structural motifs are favored for interfacial chains close to the surface. The few most favored second contacts in Fig. 6(a) at (4,7), (8,11), and (5,10) correspond to either a helix or an antiparallel sheet pattern. The most favored contacts in Figs. 6(b) and 6(c) are, respectively, (6,9) and (5,10); both of these correspond to an antiparallel sheet pattern (see Fig. 1). This is to be expected, since interfacial chains are intermediate between three-dimensional chains in the bulk and two-dimensional planar conformations, and secondary structural motifs are favored by the first pair of contacts in both two and three dimensions. At c.m. distance interval $u = 1$, the impenetrable planar surface alters significantly the topological free energy surfaces of interfacial chains in Fig. 6 from the corresponding free energy surfaces in the bulk (Fig. 2 of Ref 1, Figs. 13 and 14 in Ref 4). The quasi-two-dimensional nature of these interfacial chains is underscored by the fact that all of the most disfavored contacts in Fig. 6—(3,8), (7,12) in Fig. 6(a), (1,8), (7,14) in Fig. 6(b), and (2,9), (6,13) in Fig. 6(c)—correspond to implied blocks or prohibited contacts in two dimensions.

![Image of Figure 5](image1)

**FIG. 5.** Effects of c.m. distance $z$ from the surface on contact formation, $n = 14$. Single-contact topological free energy surface in the ensemble of interfacial conformations with (a) $1/2 < z < 5/8$ and (b) $7/8 < z < 1$ corresponding, respectively, to distance intervals $u = 0$ and $u = 3$ of Table I. Contours are given in $0.3kT$ steps. (c) Dashed horizontal lines mark the entropic free energy levels, relative to the full ensemble in the bulk, for ensembles of interfacial chains in different c.m. distance intervals. Solid curves show the variation with contact order $k$ of average entropic free energy per contact for different c.m. distance intervals. The solid curve with squares shows the variation for the full ensemble in the bulk ($z > n/2$). Except for the label "2D" for the ensemble of two-dimensional $z = 1/2$ conformations, the dashed lines and the solid curves without squares are identified by the c.m. distance label $u$ of Table I, where $(u + 4)/8 < z < (u + 5)/8$ at interval $u$.

![Image of Figure 6](image2)

**FIG. 6.** Topological free energy surfaces with a given first contact for interfacial chains with c.m. distance $5/8 < z < 3/4$ (interval $u = 1$ in Table I). (a) An order 3 contact is given; (b) an order 5 contact given; and (c) an order 7 contact is given. Contours are plotted in $0.3kT$ steps in (a) and (b) and in $0.4kT$ steps in (c). The number of conformations enumerated for (a), (b), and (c) are, respectively, 919 580, 306 992, and 139 112. Some features of these free energy surfaces are similar to the corresponding free energy surfaces of two-dimensional chains (Ref. 2).
IV. SURFACE ENHANCEMENT OF SECONDARY STRUCTURE

Does the proximity of a surface enhance the internal structure in a chain molecule? Figure 7 shows the increase in the fraction of helices, parallel and antiparallel sheets, and turns as a chain of length \( n = 14 \) approaches a surface. Let \( \tau \) label the type of secondary structure (defined in Fig. 1). The fraction of monomers \( S^{\tau \alpha}(n|z) \) in secondary structure of type \( \tau \) is computed by averaging the fraction of monomers in that secondary structure type over the ensemble of \( Q(n|z) \) interfacial \( n \)-monomer conformations at \( z \). Figure 7 shows that helices, antiparallel sheets, and turns increase monotonically as the chain c.m. approaches the surface. Parallel sheets are also enhanced near the surface, but the fraction of monomers in parallel sheets decreases when \( z \) decreases below \( z = 1 \). This is because parallel sheets in two dimensions are less favored than in three dimensions, since there are more steric constraints that chain sections connecting parallel strands must circumvent. For \( n = 14 \), the total secondary structure in the bulk and at the surface (\( \mu = 0 \) distance interval, \( 1/2 < z < 5/8 \)) are 4.49% and 12.6%, respectively. Thus the surface enhancement factor, i.e., the ratio of the maximum secondary structure fraction at or near the surface to the corresponding fraction in the bulk is 2.81 for all secondary structure types combined. While the absolute amount of secondary structure in three dimensions is less than that in two dimensions (total secondary structure for \( n = 14 \) two dimensional chains is 14.4% in the bulk and attains a maximum of 18.4% near a surface), the surface enhancement factor in three dimensions is larger than the surface enhancement factor in two dimensions. For instance, for \( n = 14 \) interfacial two-dimensional chains configured close to a linear surface, there is a maximum of a 1.27-fold increase in total secondary structure relative to chains in the bulk.

The amount of internal structure increases with the length of the polymer chain; see Fig. 8 (a). The maximum secondary fractions for interfacial chains are shown in Fig. 8 (b); these also increase with chain length.

Figure 9 shows the surface enhancement factors for all secondary structure types for three-dimensional chains as functions of chain length \( n \). While there are variations in the magnitude of surface enhancement of individual types of
secondary structure, the total secondary structure surface enhancement factor is almost constant (~2.8) throughout the range of chain lengths studied. Within the range n = 9–14, enhancement of some structural types (antiparallel sheets and turns) are more stable than the others (helices and parallel sheets). The limited exhaustive simulation data on short chains prevents us from performing accurate extrapolations of surface enhancement factors for individual structural types to large n. Nevertheless, judging from the trend shown in Fig. 9, it is reasonable to expect comparable surface enhancement to persist to longer chains, at least for total secondary structure. In any event, Fig. 8(b) strongly suggests that the absolute amount of enhanced secondary structure in interfacial molecules near or at an impenetrable surface increases with chain length. The two-dimensional model, however, suggests that the absolute amount of enhanced secondary structure in interfacial molecules near or at an impenetrable surface increases with chain length. The two-dimensional model, however, suggests that the absolute amount of enhanced secondary structure in interfacial molecules near or at an impenetrable surface increases with chain length.

V. CHAINS WITH CONTACT INTERACTIONS

In the preceding sections, we have considered self-avoiding chains at or near impenetrable surfaces in the absence of any energetic interactions. In this section, we augment this model by including two types of (spatially short-ranged) contact interactions in interfacial chains: (i) an energy $\epsilon$ for any intrachain topological contact, and (ii) an energy $\sigma$ for any chain-surface contact. In this model of interacting chains, the free energy of n-monomer chain molecules in the interfacial region with c.m. distance at $z$ is

$$\Delta G_{\nu_o}(n|z,\epsilon,\sigma) = -kT \ln \left[ \frac{\sum_{i=0}^{\nu_{\max}} \sum_{j=0}^{\nu_{\max}} Q_{\nu_o}(n|z,t,s)e^{-(\epsilon t + \sigma s)/kT}}{\sum_{i=0}^{\nu_{\max}} Q_{\nu_o}(n|z,s)e^{-\epsilon t/kT}} \right]$$

relative to chains in the bulk with the same intrachain contact energy $\epsilon$. In Eq. (5.1), $Q^{(t)}(n)$ is the number of $n$-monomer conformations in the bulk with $t$ intrachain contacts and $Q_{\nu_o}(n|z,t,s)$ is the number of interfacial (or attached) $n$-monomer conformations at $z$ with $t$ intrachain contacts and $s$ chain-surface contacts [see Eqs. (3.1)–(3.3)].

Figure 11 gives free energy as a function of $z$ for a range of chain-surface contact energies $\sigma$ for chains that are either open ($\epsilon = 0$), or compact ($\epsilon = -3kT$) in the bulk. We first consider $\epsilon = 0$ interfacial chains. For noninteracting chains $\epsilon = \sigma = 0$, free energy increases as interfacial chains approach the surface, reaching at the surface to a level of $6.4kT$ above that of chains in the bulk, as has already been noted in Sec. II. That is, in the absence of chain-surface contact energy, there is an entropic repulsion that prevents interfacial chains from approaching the surface. If there is a repulsive energy between chain monomers and the surface, the free energy at the surface is even higher relative to the bulk, for $\sigma = +1kT$ and $\epsilon = 0$, it amounts to $19.9kT$ for $n = 14$. On the other hand, the entropic repulsion from the surface can be overcome by attractive interaction between the surface and chain monomers. For chains that are open in the bulk $\epsilon = 0$, and attractive chain surface contact energy of $\sigma = -1kT$ is sufficient to give a free energy at the surface $7.26kT$ lower than that in the bulk. When the chain-surface attraction becomes stronger, at $\sigma = -3kT$, the free energy drops to $-35.1kT$ at the surface, and the free energy be-
comes significantly negative when the chain is closer to the surface than twice the bulk radius of gyration $2\sqrt{\langle R_G^2 \rangle}$. The z dependence of free energy of $s > 0$ attached chains is also shown in Fig. 11. Even in the absence of chain-surface attraction ($\sigma = 0$), the free energy increases as the c.m. of an attached chain moves away from the surface. This is a consequence of the requirement that an attached chain must contact the surface at least once. Therefore, attached chains with large z have to adopt a linearly extended configuration, thus conformational freedom is seriously restricted.

When there is sufficient intrachain attraction, chains adopt compact conformations in the bulk. For example, for $n = 14$ chains in the bulk with intrachain contact energy $\epsilon = -3kT$, the average number of intrachain contacts $\langle t \rangle = 9.81$, which translates to an average compactness $\langle \rho \rangle \equiv \langle t \rangle / \langle t \rangle_{\text{max}}$ of 0.981, since $t_{\text{max}} = 10$ for $n = 14$. In the bulk ensemble, 86% of the chains have the maximum number $t_{\text{max}}$ and 10% of the chains have the second highest number $t_{\text{max}} - 1$ of intrachain contacts. The free energy $\Delta G_i(n|z|,\sigma) + \epsilon(t)$ for $n = 14$, $\epsilon = -3kT$ interfacial chains is plotted in Fig. 11, where the constant displacement $\epsilon(t) = -29.43kT$ of the free energy $\Delta G_i$ of $\epsilon = -3kT$ chains relative to that of $\epsilon = 0$ chains is the average total intrachain contact energy of $\epsilon = -3kT$ chains in the bulk. If there is no attraction between the chain monomers and the surface, or if there is a chain-surface repulsive energy, chains that are compact in the bulk are disfavored near the surface (see the $\sigma = 0$, $+1kT$ curves in Fig. 11). However, the free energy does not rise significantly above its bulk value until the chains are much closer to the surface than that for $\epsilon = 0$ open chains. This is because the c.m. of a compact conformation can be much closer to the surface than an open conformation. When the chain-surface attraction is high ($\sigma = -3kT$), the entropic repulsion of compact conformations from the surface is overcome. An interesting feature arises when the chain-surface attraction is intermediate ($\sigma = -1kT$). As a compact chain approaches the surface, the free energy first decreases and then increases. The free energy first decreases because energetically favorable chain-surface contacts are formed when the compact conformations first touch the surface. However, further approach towards the surface is impossible without breaking some of the energetically favorable intrachain topological contacts. In the example of $n = 14$ shown in Fig. 11, no maximally compact conformations are allowed in the region $z < 1$, this accounts for the rise in free energy when z decreases below $z = 1$.

Now consider any polymeric property $f(n|z|,\sigma)$, [see Eq. (3.3)]. The dependence of $f$ on the two contact energies $\epsilon$ and $\sigma$ in the entire ensemble of interfacial or attached chains is given by the average of interfacial (i) or attached (a) conformations over all c.m. positions $1/2 < z < n/2$:

\[
\langle f(n|z|,\sigma) \rangle_{i/a} = \sum_{z = 1/2}^{n/2} \sum_{\sigma = 0}^{t_{\text{max}}} \frac{Q_{i/a}(n|z|,\sigma)}{Q_{i/a}(n)} \exp \left( - (\epsilon + \sigma)kT \right)
\]

where the notation $\Sigma_{\sigma}$ is the defined in Eq. (2.7). To compute averages in Eq. (5.2), the denominator requires the sum of conformations $\sum_{z = 1/2}^{n/2} \sum_{\sigma = 0}^{t_{\text{max}}} Q_{i/a}(n|z|,\sigma)$ over all $z$ in the interfacial region to any given $i$ and $s$. The $n = 14$ example of $\sum_{z = 1/2}^{n/2} \sum_{\sigma = 0}^{t_{\text{max}}} Q_{i/a}(n|z|,\sigma)$ is tabulated in Table II.

Figure 12 shows the properties of open and compact chains as the chain-surface attraction increases ($\sigma$ becomes more negative). For interfacial chains that adopt open conformations in the bulk ($\epsilon = 0$), both $s$ and $z$ go through relatively sharp transitions for $-1.5 < \sigma < -0.5kT$. When $\sigma$ is less than $-1.2kT$, the chains have nearly the maximum number of chain-surface contacts and the minimum c.m. distance $\langle z \rangle = 1/2$, indicating that the chains adopt essentially two-dimensional conformations on the surface, which is consistent with the free energy data shown in Fig. 11. On the other hand, the number of topological contacts $t$ does not change much with $\sigma$. In the absence of intrachain contact energy, the number of intrachain contacts for two-dimensional conformations does not differ much from that of three-dimensional conformations in the bulk (see Sec. VI). The value of $\sigma = -1.2kT$ at which the average $s$ and $z$ of interfacial chains (solid curves) and attached chains (dashed curves) bifurcate corresponds to the strength of chain-surface interaction which is sufficient to cause an overwhelming majority of interfacial chains to adhere to the surface. When the chain-surface attraction is weaker ($\sigma > -1.2kT$), the variation of $s$ and $t$ for attached chains is more gradual than that for interfacial chains. As attached chains are constrained to be close to the surface, even at $\sigma = 0$, there are more than three chain-surface contacts on average and the average c.m. is less than two bond lengths from the surface.

For interfacial chains that are compact in the bulk, the situation is very different [see Fig. 12(b) for $\epsilon = -3kT$ chains]. The principal distinction from the $\epsilon = 0$ case is the variation in the number of intrachain contacts $t$. As chain-surface attraction increases, the three-dimensional compact conformations collapse onto the surface to become conformations that are essentially two dimensional. This process is accompanied by the reduction of intrachain contacts, as the maximum number $t_{\text{max}}$ of intrachain contacts possible is higher in three dimensions than in twodimensional surfaces. When the collapse onto the surface is complete at $\sigma = -\infty$, the average compactness of $\epsilon = -3kT$ two-dimensional chains is $\langle \rho \rangle = 0.963$.

Compact chains undergo two types of transition onto the surface. First, if the chain-surface attraction is much weaker than the chain-chain attraction, then the chains can "dock" onto the surface, but without much internal deformation. Second, as the chain-surface attraction is further
TABLE II. The number of conformations $\sum_{t,s} Q_n(z,t,s)$ in the entire interfacial region $1/2 < z < n/2$ as a function of the number of intrachain topological contacts $t$ and the number of chain-surface contacts $s$. Chains with at least one surface contact $s > 0$ belong to the ensemble of attached conformations $[Eq. (3.2)]$, hence $\sum_{t,s} Q_n(z,t,s) = \sum_{t,s} Q_n(z,t,s)$ for $s > 0$. For $\varepsilon = 1/8$, a total of $\sum_{t,s} Q_n(z,t,s) = 38 935 490 822$ interfacial conformations are considered. Among them $Q_0(n) = 943 974 510$ are attached conformations, while $37 991 516 312 > 0$ interfacial conformations that do not contact the surface.

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FIG. 13. Secondary structure vs. chain-surface contact energy in a = 14 sheet fractions are shown in (a) and secondary structure types are shown in (b). Secondary structure fraction of (a) and of (b) are shown (c) and (d).}

FIG. 12. Average number of surface contacts (a) and average chain-surface contact energy (b) for interfacial chains (solid curves) and attached chains (dashed curves) with a = 14 monomers. The dependence of the number of interface contacts (c) and the dependence of the chain-surface contact energy (d) on the number of intrachain contacts (e) is also shown.
increased to be comparable to the chain–chain attraction, the surface then competes for monomers and the chain “flattens” onto the surface; see Fig. 12(b).

For the same reasons discussed above, $\epsilon = -3kT$ attached chains show a more gradual variation of properties than interfacial chains as $\sigma \to 0$. Furthermore, average attached chain c.m. distance $z$ from the surface is shorter for $\epsilon = -3kT$ chains than $\epsilon = 0$ chains, and the average number of chain–surface contacts $s$ is larger in $\epsilon = -3kT$ chains than in $\epsilon = 0$ chains at $\sigma = 0$. This is because compact chains can be configured with their centers of mass closer to an impenetrable surface than open conformations, and a smaller $z$ is correlated with a larger number of chain–surface contacts [Fig. 3(d)].

Figures 13 and 14 show the amount of internal structure as a function of the chain–surface attraction energy for $\epsilon = 0$ and 3, respectively. Because increased surface attraction leads to reduced average c.m. distance of the chain from the surface, internal structure of open chains is enhanced by surface attraction. The ensemble-averaged fraction of monomers in various secondary structure types (see Fig. 1) are defined as

$$\langle S^{(r)}(n|\epsilon,\sigma) \rangle_{\nu=0} = \frac{\sum_{z=1/2}^{n} \sum_{s=0}^{s_{\max}} S^{(r)}(n|z,s)Q_{\nu=0}(n|z,s)e^{-\epsilon - \sigma} / kT}{\sum_{z=1/2}^{n} \sum_{s=0}^{s_{\max}} Q_{\nu=0}(n|z,s)e^{-\epsilon - \sigma} / kT}.$$

(5.3)

For chains without intrachain interaction, i.e., $\epsilon = 0$ chains that adopt primarily on conformations in the bulk, there is an approximately threefold increase in total secondary structure relative to the bulk for $\sigma < -1.5kT$ [Fig. 13(a)]. While helices of type (iii), antiparallel sheets and turns are enhanced when surface attraction $-\sigma$ increases, there is a small decrease in parallel sheets, while helices of types (i), (ii), and (iv) decrease sharply once the surface attraction increases, i.e., $\sigma$ decreases beyond the value that is just sufficient to cause the majority of interfacial chains to become attached [Figs. 13(a) and 13(b)]. This is because the latter three types of helices (see Fig. 1) cannot configure on a two-dimensional square lattice, therefore they are eliminated when the chain molecules flatten onto the surface. (The monomer fractions in these three types of helices approach zero as $\sigma \to -\infty$.)

When $\sigma$ decreases below $-1.2kT$, interfacial and attached chains have essentially identical amounts of secondary structure because nearly all interfacial chains are attached to the surface for chain–surface attraction stronger than $\sigma = -1.2kT$, as indicated by Fig. 12(a). When $\sigma$ increases above $\sigma \approx -1.2kT$, the rate of decrease of total secondary structure in attached chains is more gradual than that in interfacial chains. This is because most interfacial chains will leave the surface and adopt conformations very similar to that in the bulk once the surface attraction decreases below certain critical value. On the other hand, attached chains are required to maintain contact with the surface; the full ensemble of attached conformations summed over all c.m. distances $z$ can only approach that of bulk chains when $\sigma = 0$.

When compact chains are attached, there is some enhancement of the sheet content, but no enhancement of helix content. This is accounted for by the fact that both types of structure are already significantly present in compact chains even in the absence of a surface. For the reasons discussed above, type (i), (ii), and (iv) helices are eliminated when surface attraction is strong. Despite the enhancement of helices of type (iii) as $\sigma$ decreases, the concomitant attenuation of the other three helix types results in an approximately constant amount of total helices that does not have much variation with $\sigma$. The number of turns also remains approximately constant. The approximately 30% enhancement of total secondary structure at $\sigma < -2.5kT$ relative to $\sigma = 0$ is primarily due to the enhancement of antiparallel sheets, and to a lesser degree, the enhancement of parallel sheets, which is a consequence of the fact that there are more sheets in two than in three dimensions.}

**VI. OPEN AND COMPACT POLYMERS IN THE BULK AND ON SURFACES**

In this section, we consider some approximate scaling relationships by which we can estimate the flattening transition energy$^{13-19}$ for longer chains. We first consider an $n$ monomer chain molecule with no intrachain interaction $\epsilon = 0$ that is in contact with the surface. Let the number of all accessible conformations in two and three dimensions be $Q_0^2(n)$ and $Q_0^3(n)$, respectively. $Q_0^2(n)$ corresponds to the
conformational freedom on the planar surface of the ensemble of all two-dimensional conformations, referred to here as the "two-dimensional state." \( Q_c(n) \) represents the conformational freedom of the ensemble of all attached conformations [see Eq. (2.1)], referred to as the "three-dimensional state." For an inert surface, i.e., at chain–surface contact energy \( \sigma = 0 \), the average number of chain–surface contacts \( \langle s \rangle_o \) of attached chains should be approximately proportional to the surface area of the conformation \( \langle s \rangle_o \approx K_0 n^{2/3} \), for some constant \( K_0 \), where \( K_0 \approx 1/2 \) is suggested by the exact \( n = 14 \) results in Fig. 12(a). The complete collapse of all the attached chains onto the surface (to the two-dimensional state) will cost a change (reduction) of \( k \ln \left[ Q_c^S(n)/Q_c(n) \right] \) in conformational entropy. On the other hand, the number of chain–surface contacts \( s \) will be maximized by the same process to \( s = n \). Thus on average \( n - K_0 n^{2/3} \) chain–surface contacts are made in addition to the average \( \langle s \rangle_o \) of chain–surface contacts present among noninteracting attached molecules in the three-dimensional state. In order that the two-dimensional state is favored, the gain in entropic free energy must be overcompensated by the decrease in contact energy supplied by the additional chain–surface contacts. Hence a chain–surface contact energy that is more negative, i.e., more strongly attractive, than the critical value

\[
\sigma_0 = \frac{kT}{n - K_0 n^{2/3}} \ln \left[ \frac{Q_c^S(n)}{Q_c(n)} \right] = \frac{n kT}{n - K_0 n^{2/3}} \ln \left( \frac{\mu_2}{\mu_3} \right)
\]

is required to favor collapse of attached chains onto the surface. The last equality in Eq. (6.1) is obtained by using the large \( n \) formulas\(^{20} \) and \( Q_c^S(n) \sim n^{2/3} \mu_2 \), \( Q_c(n) \sim n^{2/3} \mu_2 \), and neglecting terms of order \( (\ln n)/n \) and \( 1/n \). Exact lattice simulations give \( \mu_2 \approx 2.64 \) for two-dimensional square lattices and \( \mu_2 \approx 4.68 \) for three-dimensional simple cubic lattices.\(^{2,4} \) Application of the first equality in Eq. (6.1) with \( K_0 = 1/2, Q_c^S(n) = 881 500, \) and \( Q_c(n) = 943 974 \) results in \( n = 14 \) chains yields \( \sigma_0 = -0.63 kT \), which corresponds approximately to the value of \( \sigma \) in Fig. 12(a) at the midpoint of the transition of attached chains from three-dimensional to two-dimensional conformations. The last term in Eq. (6.1) is plotted in Fig. 15 which shows the critical chain–surface contact energy \( \sigma_0 \) for chain lengths \( n < 1000 \), computed using \( K_0 = 1/2 \) and the values of \( \mu_2 \) and \( \mu_3 \) for square and cubic lattices. \( \sigma_0 \) shows very little variation with chain length, \( \sigma_0 \approx -0.66 kT \) throughout the entire range of \( n \) plotted. In the infinite chain length limit, \( n \rightarrow \infty \), \( \sigma_0 \) for \( \epsilon = 0 \) chains approaches \( kT \ln (\mu_2/\mu_3) = -0.57 kT \).

It is noteworthy that the transition energy estimated here for excluded-volume chains with at least one monomer attached to the surface approximately coincides with some of the earlier estimates of the transition energies for terminally attached chains with excluded volume. For instance, the latter was estimated by Ishinabe\(^{18} \) using exact enumerations on tetrahedral and simple cubic lattices to be in the range between \(-0.60 \) and \(-0.45 kT \), and Eisenriegler, Kremer, and Binder\(^{17} \) obtained \(-0.44 kT \) for the corresponding transition energy by Monte Carlo simulations on tetrahedral lattices.

Polymers have compact\(^{3,4} \) conformations when their intrachain attraction is strong. We now consider a chain molecule whose \(- \epsilon \) is sufficiently large that the overwhelming majority of both its two- and three-dimensional conformations are maximally compact, i.e., with \( t = t_{\text{max}} \) and \( t = t_{\text{max}} \) where \( t_{\text{max}} \) and \( t_{\text{max}} \) are the maximum number of intrachain contacts that characterize the total number \( Q_c^S(n) \sim k_2 \) and \( Q_c(n) \sim k_2 \) of maximally compact \( n \)-monomer conformations in two and three dimensions, respectively. Exhaustive simulations give \( k_2 \approx 1.41 \) for square lattices\(^{3} \) and \( k_3 \approx 1.74 \) for simple cubic lattices.\(^{4} \) In the absence of chain–surface interaction, i.e., at \( \sigma = 0 \), three-dimensional compact conformations in contact with the surface on average should have \( \langle s \rangle_c \approx n^{2/3} \) chain–surface contacts. Hence additional \( n - n^{2/3} \) chain–surface contacts are made when the transition to the compact two-dimensional state is completed. The change in entropy in the transition from three- to two-dimensional conformations is \( k \ln \left[ Q_c^S(n)/Q_c(n) \right] \) and the change in the total intrachain contact energy is \( \epsilon (t_{\text{max}} - t_{\text{max}}) \), since \( t_{\text{max}} \neq t_{\text{max}} \) for \( n > 7 \) (see Refs. 3 and 4). The latter effect is specific to compact polymers. The combined contribution from these factors implies the critical chain–surface contact energy

\[
\sigma_c = \frac{1}{n - n^{2/3}} \left[ kT \ln \left( \frac{Q_c^S(n)}{Q_c(n)} \right) + \epsilon (t_{\text{max}} - t_{\text{max}}) \right]
\]

\[
= \frac{1}{n - n^{2/3}} \left[ nkT \ln \left( \frac{k_2}{k_3} \right) + \epsilon (t_{\text{max}} - t_{\text{max}}) \right]
\]

for compact polymers. Application of Eq. (6.2a) to \( n = 14 \), with \( Q_c^S(n) = 2880 \) and \( Q_c(n) = 124 128 \), gives \( \sigma_c = -1.56 kT \), which corresponds approximately to the midpoint of the three- to two-dimensional transition of at-
tached chains shown in Fig. 12(b). $\sigma$ for chain lengths up to 1000 are computed by Eq. (6.2b) and plotted in Fig. 15 for three values of $\epsilon = -1$, $-2$, and $-3kT$. In the limit of infinite chain length, $t_{\text{max}}^{(2)} \sim n$, $t_{\text{max}}^{(3)} \sim 2n$, therefore

$$\lim_{n \to \infty} \sigma = \left[ kT \ln \left( \frac{\kappa_2}{\kappa_3} \right) + \epsilon \right] = -0.21kT + \epsilon \quad (6.3)$$

and $\sigma < \epsilon$. However, it is possible that $\sigma > \epsilon$ for smaller $n$ because monomers situated on the conformational surface (not to be confused with the impenetrable planar surface) make fewer intrachain contacts than those in the interior, and this "conformational surface effect" cannot be neglected when $n$ is small.

We now ask: what magnitude of $\epsilon$ is sufficient to cause chain molecules to adopt compact conformations? To simplify the notation, let $Q_c$ and $Q_o$ be the number of all accessible (i.e., open) conformations and all maximally compact conformations in two or three dimensions, $\langle t \rangle$ be the average number of intrachain contacts in the open state, and $t_{\text{max}}$ be the maximum number of intrachain contacts in the compact state. Thus the change in entropy in going from the open to the compact state is $k \ln (Q_c/Q_o)$. For the compact state to be favorable, the loss in entropy must be overcompensated by the gain in intrachain contact energy, which is given by $\epsilon(t_{\text{max}} - \langle t \rangle)$. Hence the critical intrachain contact energies $\epsilon_2$ and $\epsilon_3$ for the transition between the open and compact polymeric states in two and three dimensions are, respectively,

$$\epsilon_2 = \frac{kT}{t_{\text{max}}^{(2)} - \langle t \rangle^{(2)}} \ln \left[ \frac{Q_c(n)}{Q_o(n)} \right]$$

(6.4)

and

$$\epsilon_3 = \frac{kT}{t_{\text{max}}^{(3)} - \langle t \rangle^{(3)}} \ln \left[ \frac{Q_c(n)}{Q_o(n)} \right] = \frac{n kT}{t_{\text{max}}^{(3)} - \langle t \rangle^{(3)}} \ln \left( \frac{\kappa_3}{\mu_3} \right) \quad (6.5)$$

Exact results from exhaustive simulations of short chains in two and three dimensions consistently show that chain molecules with the critical intrachain contact energies $\epsilon_2$ and $\epsilon_3$ are indeed intermediate between open and compact. Every exact average compactness$^3$ at $\epsilon_2$ of two-dimensional chains exhaustively simulated for $n = 9\text{--}20$ falls between 0.71 and 0.76; every exact average compactness at $\epsilon_3$ of three-dimensional chains exhaustively simulated for $n = 9\text{--}14$ falls between 0.62 and 0.68.

Results from exhaustive simulations of short chains are extrapolated to estimate the quantities $\langle t \rangle^{(2)}$ and $\langle t \rangle^{(3)}$ in Eqs. (6.4) and (6.5) for long chains. For this purpose, the infinite chain length $n \to \infty$ limit of $\langle t \rangle^{(2)}/n$ and $\langle t \rangle^{(3)}/n$ in two$^4$ and three$^2$ dimensions are considered, which are, respectively, estimated to be approximately $0.16$ and $0.19$. These limiting relations are substituted into Eqs. (6.4) and (6.5) to yield $\epsilon_2$ and $\epsilon_3$ at long chain lengths, plotted in Fig. 15. The figure shows that $\epsilon_2$ and $\epsilon_3$ for small $n$ are more negative than their $n \to \infty$ limits $\epsilon_2 \to -0.75kT$ and $\epsilon_3 \to -0.55kT$. As for the variation of $\sigma$ described above, this is a consequence of the "conformational surface effect." However, for $n > 200$, the critical intrachain contact energies $\epsilon_2$ and $\epsilon_3$ show only very gradual variations. The values of $\epsilon_2$ and $\epsilon_3$ are comparable throughout a wide range of chain lengths, which implies that a chain molecule with sufficient intrachain attraction to become compact in two dimensions is likely to also be compact in three dimensions, and vice versa.

According to the Flory mean-field theory,$^{23}$ the ratio of the number of compact to all accessible conformations per chain segment $(\kappa_2/\mu_2)$ and $(\kappa_3/\mu_3)$ in both two and three dimensions may be approximated by the inverse of the base of natural logarithm $e^{-1} = 0.3678...$ for chains configured in any lattice.$^{23,24}$ Moreover, for sufficiently long chain lengths, the ratio $t_{\text{max}}^{(2)}/t_{\text{max}}^{(3)}$ deduced from square and cubic lattice considerations essentially reflects only the difference in coordination number in two and three dimensions, hence it should be a good approximation of the corresponding ratio in more general chain configurations not necessarily confined to specific lattices. Insofar as these premises are valid, the ratio of transition contact energies in two and three dimensions, $\epsilon_2/\epsilon_3$, which can easily be deduced from results above for square and cubic lattice chains, may be a reasonable approximation of the corresponding ratio for chains configured in two and three dimensions in general.

VII. CONCLUSIONS

We have considered the conformations of chain molecules at or near impenetrable interfaces. We have explored how the conformations depend on the distance of the center of mass of the chain from the surface, by exhaustive enumeration for short chains on three-dimensional simple cubic lattices. We find that the conformational ensemble becomes restricted as the chain approaches the surface; hence there is an entropic repulsion and the conformations become distorted as they flatten onto the surface. We observe that as the chain approaches a surface, there is an enhancement of certain conformational patterns, namely, helices, turns, and parallel and antiparallel sheets. We consider homopolymers here, for which this enhancement is statistical; it is possible that copolymers with specific monomer sequences, such as those occurring in proteins and peptides, might be induced to unique conformations by the presence of a surface. In this work, we consider homopolymer chains in an ideal solvent (intrachain interaction equals to 0) and homopolymer chains in a very poor solvent (intrachain interaction equals to $-3kT$ per monomer–monomer contact). The latter is largely the class of maximally compact conformations. With increasing surface-chain attraction, the chains in ideal solvents undergo a flattening transition onto the surface. On the other hand, with increasing surface-chain attraction, the compact chains first undergo a "docking" transition in which the compact polymer sticks rigidly to the surface with little internal deformation, then a "flattening" transition in which it undergoes a transition from three to two dimensions.

ACKNOWLEDGMENTS

We thank the NSF, NIH, and the URI program of DARPA for research support. M.W. and V.B. thank the
Minnesota Supercomputer Institute for providing computer time. We thank an anonymous referee for helpful comments.

6In Ref. 5, the distance $y$ between the chain c.m. and the surface is defined as the separation between the $y$ coordinate of the c.m. and the $y$ coordinate of the center of any lattice sites that are in contact with the surface, hence the separation defined in Ref. 5 is equivalent to the separation defined here minus $1/2$.
7Note that $Q_0(n)$ here is a function of the number of monomers $n$, while $Q_0(N)$ in Ref. 4 is a function of the number of bonds $N = n - 1$.
8$Q_0^f(n)$ is given by $8\Omega_0(N) - 4$ for $N = n - 1$, where $\Omega_0(N)$ is defined in Refs. 2 and 3 (see footnote 23 of Ref. 3 for details).
12Note that the total number of conformations in the interfacial region depends on the c.m. distance interval width $\delta z$ in the present model. Good resolution of $z$ dependence of polymeric properties requires a small $\delta z$. On the other hand, an infinitesimal $\delta z$ is unphysical, as $\delta z$ reflects the spatial range of the model chain-surface interaction. A displacement of $\delta z$ of an adsorbed chain from the surface should bring the monomers previously in contact with the surface beyond the short range of contact interaction [see Eq. (3.2)].
23P. J. Flory, Principles of Polymer Chemistry (Cornell University, Ithaca, New York, 1953).