A Direct Enumeration Study of Self-Avoiding Walks Terminally Attached to a Surface

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Received May 30, 1973

ABSTRACT: A study of the behavior of self-avoiding walks which contact a surface only at their end points has been performed by directly enumerating self-avoiding chains of size $N \leq 14$ on the diamond lattice. Both loop and open configurations were studied. It was found that for open chains the surface effect is small in the absence of an interaction energy. Moreover the ratio, $\langle S^2_N \rangle / \langle R^2_N \rangle$ (the ratio of the mean-square radius of gyration to the mean-square end-to-end distance) for open chains was found to approach 0.1314 while the same ratio for random returning loops approaches 0.200 as $N \to \infty$. An estimate for the index β in the expression for the probability for return to the surface $P_N \sim N^{-\beta}$ is also given. It is also found that both $\langle R^2_N \rangle$ and $\langle S^2_N \rangle$ for open configurations increase rapidly above a critical energy with increasing interaction with the surface, while these same configurational properties for loops increase continuously with increasing surface interaction.

Various analytical theories have been presented to describe the behavior of adsorbed polymer molecules.[1-8] However much less attention has been focused on the mean dimensions of terminally adsorbed chains. By terminally adsorbed one means that the chain is only attached to the surface at one or both of its ends (see Figure 1). This particular model of an adsorbed polymer chain yields information on entropy effects involved in the chain folding of polymer crystals, on configurational effects of polymer chains in stabilizing colloidal dispersions and on the relative importance of chain ends and internal loops on the adsorption characteristics of totally adsorbed polymers. In general an adsorbed polymer chain consists of the following chain types; *loops* (which project into the three-dimensional space of the solution), *surface trains* (running along the two-dimensional plane of the surface), and *open chains* (projecting into the three-dimensional space of the solution). The behavior of surface trains is a two-dimensional problem which has been studied previously.[9-11] However the behavior of open chains and loops has received little attention. Recently Hesselink[12] and Meier[13] have studied such a model analytically using random walk statistics.

A much more complicated but more realistic approach would consider the effect of excluded volume caused by polymer–polymer and polymer–surface interactions. In the past few decades high-speed digital computers have been used with success to study the configurational behavior of macromolecules. In particular McCrackin[14] and Clayfield and Lumb[15] have used Monte Carlo techniques to simulate adsorbed polymers. In addition Lax[16] has used the exact enumeration method to obtain information regarding self-avoiding chain dimensions near surfaces. In this paper the configurational behavior of *open* self-avoiding terminally attached chains (*i.e.*, those chains which initiate on a surface but never return to it) and *closed* self-avoiding terminally attached chains (*i.e.*, loops which return to the surface for the first time) are reported from an analysis of data obtained from the exact enumeration of non-self-intersecting walks generated on the diamond lattice in the presence of a solid surface.

I. Method

The technique for the enumeration of self-avoiding chains has been adequately described.[16,17] All programs were written in Fortran IV and run on the Golem A computer, located in the Department of Applied Mathematics of the Weizmann Institute of Science. The plane $Z = 0$ was defined as the solid surface. Non-self-intersecting walks of size $N \leq 14$ on the diamond lattice were generated subject to the following additional constraints. All walks were initialized on the surface $Z = 0$; no walk penetrated the space below the plane $Z = 0$; chains were only permitted to touch the surface at their end points. Interaction of the chains with the surface was considered in the following manner. The number of contacts for a given chain with the plane $Z = 1$, n_i (*i.e.*, a nearest-neighbor interaction), was recorded. Each contact contributed a factor ϵ to the chain energy. An average configurational property of the chains for a walk of size N, $\langle P_N \rangle$, is then given by

$$\langle P_N \rangle = \frac{\sum_{i=1}^{C_N} P_i \exp(-n_i \epsilon / KT)}{\sum_{i=1}^{C_N} \exp(-n_i \epsilon / KT)} \qquad (1)$$

where K is the Boltzmann constant, T the absolute temperature, and C_N the total number of chains generated.

II. Results and Discussion

A. Configurational Properties: Energy Dependence. Figure 2 is a plot of the mean-square end-to-end distance of open (no return to the surface) chains, $\langle R^2_N \rangle_{nr}$ as well as the mean-square end-to-end distance of (random return to the surface) loops, $\langle R^2_N \rangle_{rr}$, *vs.* the interaction energy ϵ. A number of important features of the curves are apparent. $\langle R^2_N \rangle_{rr}$ does not decrease at all as ϵ increases but expands smoothly with the elongation of the loop sections proceeding at a faster rate than that of the open chain sections for $\epsilon < -1.4KT$. Also, initially ($\epsilon = 0$) $\langle R^2_N \rangle_{rr}$ is about 57% of the magnitude of $\langle R^2_N \rangle_{nr}$. The behavior of the open chains is similar to that reported by Rubin[18] for the random walk case.

Figure 3 shows the mean-square radius of gyration of open chains $\langle S^2_N \rangle_{nr}$, as well as the mean square radius of gyration of loops $\langle S^2_N \rangle_{rr}$ as a function of the interaction ϵ. The mean-square radius of gyration of loops shows no decrease in the critical region[14,18] and increases smoothly and rapidly with ϵ. $\langle S^2_N \rangle_{nr}$ behaves in a similar manner as $\langle R^2_N \rangle_{nr}$.

Figure 4 is a plot of the average maximum normal to the surface distance of open chains $\langle Z^{max}_N \rangle_{nr}$ and loops $\langle Z^{max}_N \rangle_{rr}$ as a function of ϵ. It is quite obvious from this plot that open chains extend out to greater distances into the solution than loops of the same size. Moreover in conjunction with the information on $\langle R^2_N \rangle_{nr}$, $\langle S^2_N \rangle_{nr}$ and $\langle R^2_N \rangle_{rr}$, $\langle S^2_N \rangle_{rr}$, one may obtain deeper insight into the interaction mechanism. Firstly, as far as open chains are concerned in the region $\epsilon \leq -1.0KT$, $\langle Z^{max}_N \rangle_{nr}$ decreases

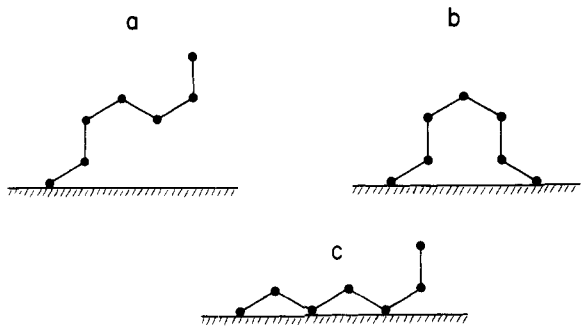

Figure 1. Some chain topologies near a solid surface: (a) open chain; (b) loop; (c) heavily attached.

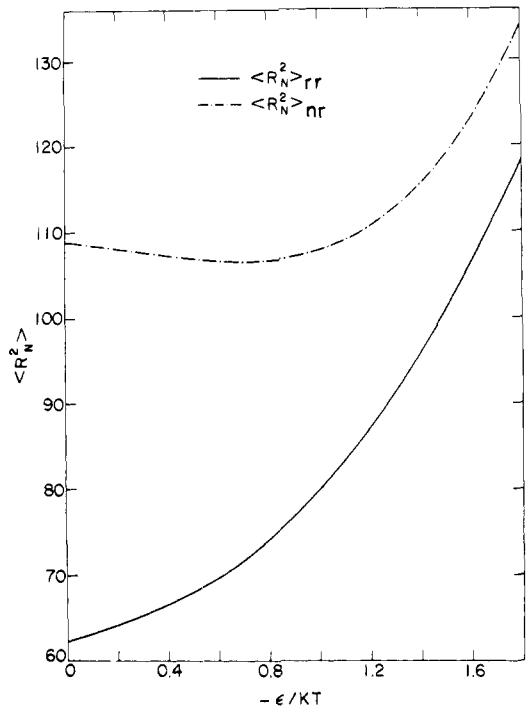

Figure 2. Plot of the mean-square end-to-end distance of open chains, and loops for chains of size $N = 14$ *vs.* the interaction energy.

while $\langle R^2_N \rangle_{nr}$ and $\langle S^2_N \rangle_{nr}$ are slightly decreasing. This implies that the chain is collapsing downward toward the surface and inward toward itself. Loops, on the other hand, have $\langle Z^{max}_N \rangle_{rr}$ decreasing while $\langle R^2_N \rangle_{rr}$ and $\langle S^2_N \rangle_{rr}$ are both increasing indicating that as soon as interaction begins the loop regions collapse downward toward the surface while at the same time expand parallel to it. Secondly, for energies greater than $-1.0KT$, both loops and chains continue to be drawn toward the surface while at the same time expand parallel to it. This proposal is consistent with that suggested previously.[16]

Figure 5 is a plot of the ratio of the mean-square radius of gyration to the mean-square end-to-end distance of chains which randomly return to the surface, $\langle S^2_N \rangle_{rr}/\langle R^2_N \rangle_{rr}$, and those that do not at all return to the surface, $\langle S^2_N \rangle_{nr}/\langle R^2_N \rangle_{nr}$, as a function of ϵ. The constancy of $\langle S^2_N \rangle_{nr}/\langle R^2_N \rangle_{nr}$ up to $\epsilon \simeq -1.6KT$ suggests that this ratio is probably independent of surface interactions in this region. Furthermore it further implies that both $\langle S^2_N \rangle_{nr}$ and $\langle R^2_N \rangle_{nr}$ have a similar type of ϵ dependence, which is seen to be true from Figures 2 and 3. The fact that the ratio for loops, $\langle S^2_N \rangle_{rr}/\langle R^2_N \rangle_{rr}$, drops off suddenly with increasing ϵ implies that $\langle R^2_N \rangle_{rr}$ is increasing more rapidly than $\langle S^2_N \rangle_{rr}$ with ϵ.

B. Configurational Properties: Molecular Weight Dependence. 1. Open Chains. Table I lists some configurational properties for chains which have no returns to the surface as a function of N for $\epsilon = 0$. Previous studies of self-avoiding lattice walks near barriers[15,16] have shown that

$$\langle R^2_N \rangle \simeq AN^{\gamma} \tag{2}$$

and that asymptotic estimates for γ are obtainable by application of the ratio method[16] which gives the following approximate equation for finite γ

$$\gamma_N \simeq N[(\langle R^2_{N+1} \rangle/\langle R^2_N \rangle) - 1] \tag{3}$$

From a plot of γ_N *vs.* $1/N$ extrapolated to $1/N = 0$, one

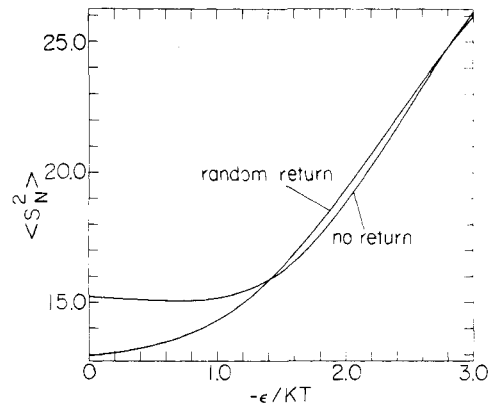

Figure 3. Plot of the mean-square radius of gyration of open chains, and loops for chains of size $N = 14$ *vs.* the interaction energy.

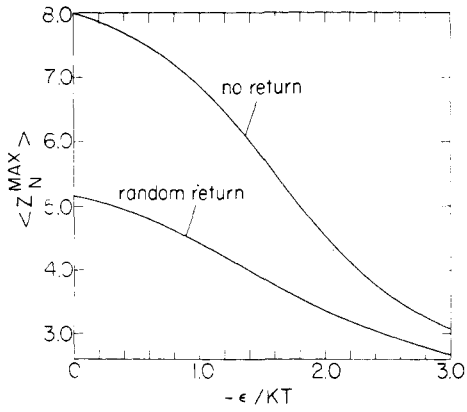

Figure 4. Plot of the average maximum normal to the surface distance of open chains and loops for chains of size $N = 14$ *vs.* the interaction energy.

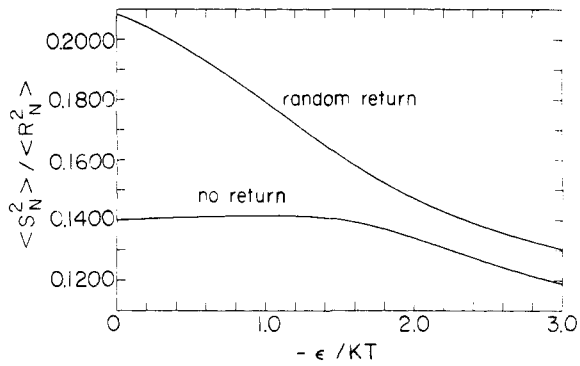

Figure 5. Plot of the ratio of the mean-square radius of gyration to the mean-square end-to-end distance of open chains and loops for chains of size $N = 14$ *vs.* the interaction energy.

Table I[a]

N	C_N^{nr}	$\langle R^2_N\rangle_{nr}$	$\langle S^2_N\rangle_{nr}$	$\langle S^2_N\rangle_{nr}/\langle R^2_N\rangle_{nr}$	$\langle Z_N^{max}\rangle_{nr}$	$\langle Z_N\rangle_{nr}$
2	2	8.0000	1.5556	0.19444	2.00000	2.00000
3	6	13.6667	2.4167	0.17683	2.66667	2.33333
4	14	21.7143	3.4629	0.15947	3.42857	3.14286
5	42	28.1429	4.4431	0.15788	3.90476	3.28571
6	106	36.9811	5.5803	0.15090	4.56604	3.96226
7	314	43.8662	6.6226	0.15097	4.94268	4.08280
8	818	53.5355	7.8304	0.14626	5.52567	4.69927
9	2398	60.9883	8.9438	0.14665	5.87656	4.80651
10	6374	71.2620	10.2170	0.14337	6.41167	5.37120
11	18638	78.9687	11.3673	0.14395	6.73463	5.46529
12	50250	89.6716	12.6826	0.14143	7.23009	5.98838
13	146438	97.7187	13.8770	0.14201	7.53198	6.07775
14	398754	108.7960	15.2320	0.14001	7.99713	6.56759

[a] A list of the number of open–no return to the surface (nr) terminally adsorbed chains, C_N^{nr}; their mean-square end-to-end distance, $\langle R^2_N\rangle_{nr}$; mean-square radius of gyration, $\langle S^2_N\rangle_{nr}$; ratio of the mean-square radius of gyration to the mean square end-to-end distance, $\langle S^2_N\rangle_{nr}/\langle R^2_N\rangle_{nr}$; average maximum normal to the surface distance of the chains, $\langle Z^{max}{}_N\rangle_{nr}$; and average normal distance to the surface of the chain ends, $\langle Z_N\rangle_{nr}$; in the absence of a surface interaction ($\epsilon = 0$). All the C_N^{nr} values listed are reduced by a factor of two due to symmetry considerations.

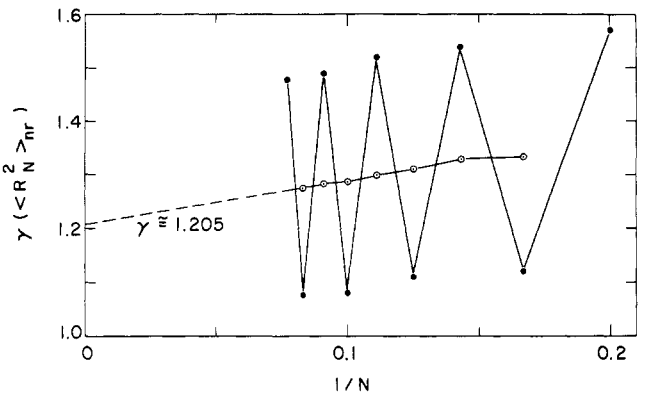

Figure 6. Plot of $\gamma(\langle R^2_N\rangle_{nr})$ *vs.* $1/N$ for $\epsilon = 0$.

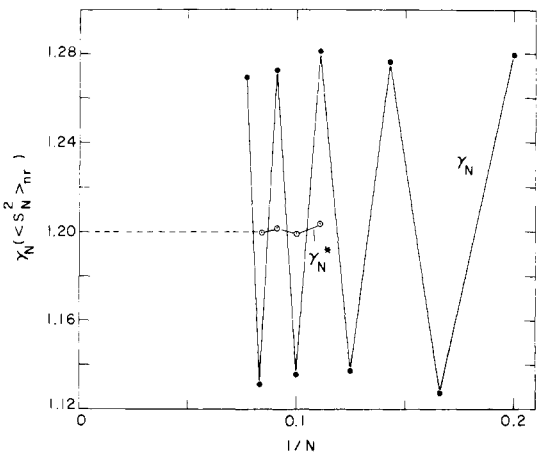

Figure 7. Plot of $\gamma(\langle S^2_N\rangle_{nr})$ *vs.* $1/N$ for $\epsilon = 0$.

can obtain an estimate of γ_∞. Figure 6 is such a plot for $\langle R^2_N\rangle_{nr}$ when $\epsilon = 0$. Fluctuation in the γ_N values was reduced by averaging the γ_N, *i.e.*

$$\gamma_N^* = (1/2)(\gamma_N + \gamma_{N+1}) \tag{4}$$

The γ_N^* values are well behaved, yielding a limiting exponent of $\gamma \simeq 1.205$. This estimate for the exponent is in excellent agreement with that reported by Kumbar and Windwer[19] from their study of self-avoiding walks on the diamond lattice in the absence of a barrier. It seems that the barrier has little effect on $\langle R^2_N\rangle_{nr}$ when $\epsilon = 0$. Some indication as to the trend in the exponent with increasing

Table II
Limiting Estimates for Exponent γ_∞ in Equation 2 and the Ratio of the Mean-Square Radius of Gyration to the Mean-Square End-to-End Distance for Open Chains as a Function of the Interaction Energy

$-\epsilon/KT$	$\gamma_\infty(\langle R^2_N\rangle_{nr})$	$\langle S^2_N\rangle_{nr}/\langle R^2_N\rangle_{nr}$
0.0	1.20	0.1314
0.1	1.21	0.1313
0.3	1.19	0.1327
0.5	1.20	0.1344
0.7	1.18	0.1353
0.9	1.18	0.1366
1.1	~1.15	0.1383
1.3	~1.16	0.1392
1.5	~1.22	0.1387
1.7	~1.31	0.1345

adsorption energy was obtained by treating the even and odd series separately, *i.e.*

$$\gamma_N \simeq (N/2)[\langle R^2{}_{N+2}\rangle_{nr}/\langle R^2{}_N\rangle_{nr}) - 1] \tag{5}$$

and

$$\gamma_N^* = (1/2)(\gamma_N + \gamma_{N+2}) \tag{6}$$

the estimates for $\gamma_\infty(\epsilon)$ are listed in Table II. A decrease in γ_∞ is noted in the region $-0.5KT > \epsilon > -1.5KT$. Since such behavior was reported previously,[16] it seems worthwhile to study this region with Monte Carlo techniques to obtain data on longer chains. The possibility of $\gamma = 1.0$ somewhere in the energy interval $-0.9KT \rightarrow -1.3KT$ certainly still appears to be a realistic possibility.

Results for $\langle S^2_N\rangle_{nr}$ are most encouraging. Assuming that

$$\langle S^2_N\rangle_{nr} = A'N^{\gamma'} \tag{7}$$

one estimates γ' using the ratio method (eq 2 and 3). Figure 7 is a plot of γ'_N and $\gamma'_N{}^*$ for $\epsilon = 0$. It is seen that $\gamma'_N \rightarrow 1.20$ as $N \rightarrow \infty$. Fluctuations in $\gamma'_N{}^*$ are further minimized by forming

$$\gamma'_N{}^{**} = (1/2)(\gamma'_N{}^* + \gamma'_{N+1}{}^*) \tag{8}$$

The following values were computed for $\gamma'_N{}^{**}$: $\gamma'_7{}^{**} = 1.2082$, $\gamma'_8{}^{**} = 1.2065$, $\gamma'_9{}^{**} = 1.2015$, $\gamma'_{10}{}^{**} = 1.2004$, and $\gamma'_{11}{}^{**} = 1.2006$; estimating γ' as 1.20 extremely well. Estimation of the limiting value for γ' with increasing

Table III[a]

N	C_N^{rr}[b]	$\langle R^2_N\rangle_{rr}$	$\langle S^2_N\rangle_{rr}$	$\langle S^2_N\rangle_{rr}/\langle R^2_N\rangle_{rr}$	$\langle Z^{max}{}_N\rangle_{rr}$
2	1	8.00000	1.55556	0.19444	1.00000
4	4	12.00000	2.80000	0.23333	2.00000
6	18	22.22222	4.70748	0.21184	2.77778
8	106	30.33962	6.54927	0.21587	3.47170
10	638	40.85266	8.62485	0.21112	4.07210
12	4,126	51.10616	10.75050	0.21036	4.64033
14	27,474	62.24765	12.97201	0.20839	5.17398

[a] A list of the number of loops, C_n^{rr}, which randomly return to the barrier, their mean-square end-to-end distance, $\langle R^2_N\rangle_{rr}$; their mean-square radius of gyration, $\langle S^2_N\rangle_{rr}$; the ratio of the mean-square radius of gyration to the mean-square end-to-end distance, $\langle S^2_N\rangle_{rr}/\langle R^2_N\rangle_{rr}$; and the average maximum normal to the surface distance of the loops $\langle Z^{max}{}_N\rangle_{rr}$ as a function of N for $\epsilon = 0$. [b] A symmetry factor of 2 was used here.

values of ϵ was not possible (except for $0.0 \leq \epsilon \leq -0.3KT$) since curvature was observed in the plot of $\gamma'_N{}^*$ *vs.* $1/N$. The slower convergence of the mean-square radius of gyration as compared with the mean-square end-to-end distance for short chains has been noted in earlier studies.[19,20]

A result which is deemed significant is the limiting values for the ratio $\langle S^2_N\rangle_{nr}/\langle R^2_N\rangle_{nr}$. As stated in an earlier paper,[16] this ratio was found not to be approaching 0.155 ± 0.002, the value obtained from Monte Carlo[21] as well as exact enumeration studies[11] on self-avoiding lattice walks in the absence of a barrier. Further support for the deviation of this ratio from the accepted bulk value is now reported. Figure 8 is a typical plot of $\langle S^2_N\rangle_{nr}/\langle R^2_N\rangle_{nr}$ *vs.* $1/N$ extrapolated to $1/N = 0$. The curve is well behaved (linear) reaching a limiting value 0.1314. Table II lists the estimate of lim $(N \to \infty)$ $\langle S^2_N\rangle_{nr}/\langle R^2_N\rangle_{nr}$ for some values of ϵ. All the values reported in Table II were obtained from extrapolation of very well behaved curves similar to that shown in Figure 8. The consistency of the limiting value of this ratio with increasing ϵ implies that both $\langle R^2_N\rangle_{nr}$ and $\langle S^2_N\rangle_{nr}$ behave functionally the same with N, and it seems logical that eq 2 and 7 describe that behavior adequately, at least when $\epsilon = 0$. It would be useful to examine the amplitudes A and A' listed in eq 2 and 7 as a function of N. Assuming the exponent in eq 2, $\gamma = 1.20$, and the exponent in eq 7, $\gamma' = 1.20$, the A_N's are given by

$$A_N = \langle R^2_N\rangle_{nr}/N^{1.20} \tag{9}$$

and

$$A_N' = \langle S^2_N\rangle_{nr}/N^{1.20} \tag{10}$$

A plot of A_N and A_N' *vs.* $1/N$ extrapolated to $1/N = 0$ gives estimates for A and A'. Figure 9 shows the result for A_N and A_N' *vs.* $1/N$, when $\epsilon = 0$. Aside from the normal oscillations observed for the data one estimates that

$$A' \simeq 0.636 \qquad N \to \infty \tag{11}$$

and similarly

$$A \simeq 4.80 \qquad N \to \infty \tag{12}$$

Domb[9] gives the following equations for the behavior of the end-to-end distance for the diamond lattice in the absence of a barrier,

$$\langle R^2_N\rangle = 1.2875N^{6/5} - 0.2705 \tag{13}$$

It is seen that a significant change in the amplitude has occurred by the introduction of a solid surface.

In the absence of surface attraction it was found that, $\langle Z^{max}N\rangle_{nr} \propto N^{0.628}$ and $\langle Z_N\rangle_m \propto N^{0.610}$. With increasing ϵ, the normals to the surface distances were found to be converging too slowly to obtain estimates of the exponent describing their molecular weight behavior.

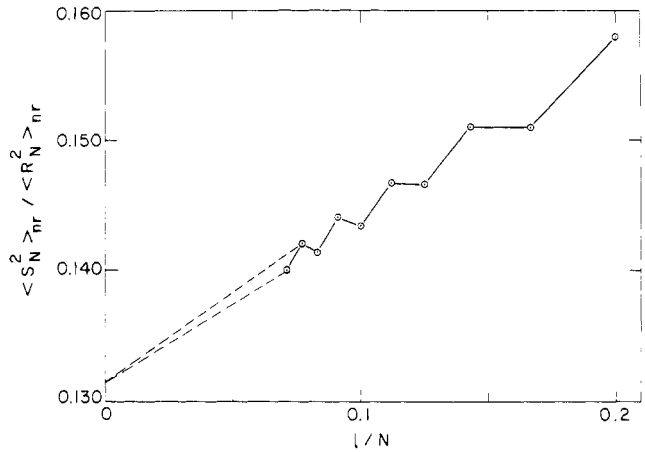

Figure 8. Plot of the ratio of the mean-square radius of gyration to the mean-square end-to-end distance of open chains *vs.* $1/N$ for $\epsilon = 0$.

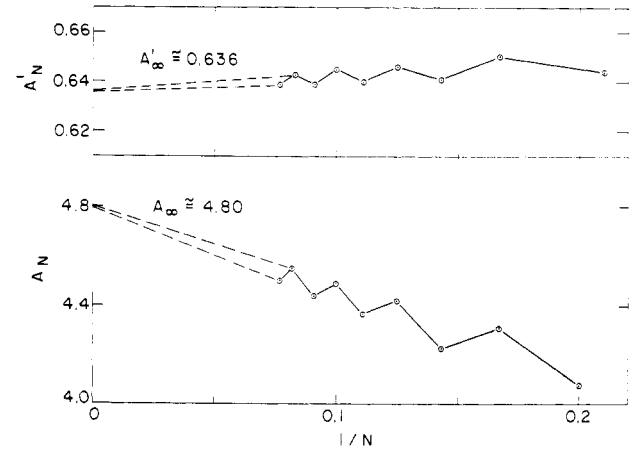

Figure 9. Plot of the amplitudes in eq 9 and 10 *vs.* $1/N$ for $\epsilon = 0$.

2. Loops. Table III lists the value for some configurational properties of loops which *randomly return* to the barrier, while Table IV lists values for some configurational properties of loops which *return adjacent* to the initial point as a function of N. It is known from previous investigation[19,22] that the radius of gyration of rings (*i.e.*, configurations which return to the origin) obeys eq 7 and the meagre evidence that is available indicates that the exponent is $\frac{6}{5}$ in three dimensions. The following values for $\gamma_N(\langle S^2_N\rangle_{rr})$ were obtained using eq 5: $\gamma_2 = 0.7999$, $\gamma_4 = 1.3625$, $\gamma_6 = 1.1739$, $\gamma_8 = 1.2677$, $\gamma_{10} = 1.2323$, $\gamma_{12} = 1.2400$. Extrapolation was not attempted; however, the sequence seems to be converging slowly to $\gamma \sim 1.230$. The similar sequence for $\gamma_N(\langle S^2_N\rangle_{ar})$ is: $\gamma_2 = 0.697$, $\gamma_4 =$

Table IV[a]

N	C_N^{ar}[b]	$\langle S^2_N\rangle_{ar}$	$\langle Z^{max}{}_N\rangle_{ar}$
2	1	1.5556	1.0000
4	2	2.6400	2.0000
6	6	3.5646	3.0000
8	22	4.8171	3.7273
10	106	5.8971	4.3774
12	506	7.2837	4.9605
14	2774	8.5451	5.5609

[a] A list of the number of loops of size N, C_N^{ar} which return adjacent to the initialization point on the barrier; their mean square radius of gyration, $\langle S^2_N\rangle_{ar}$; and their average maximum normal distance to the barrier, $\langle Z^{max}{}_N\rangle_{ar}$, as a function of N for $\epsilon = 0$. [b] A symmetry factor of two was used here.

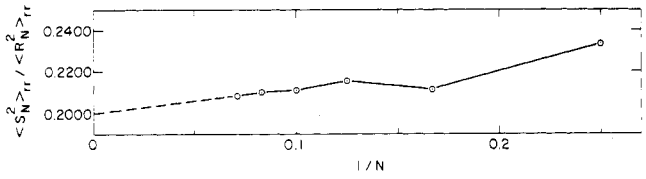

Figure 10. Plot of the ratio of the mean-square radius of gyration to the mean-square end-to-end distance of random returning loops *vs.* $1/N$ for $\epsilon = 0$.

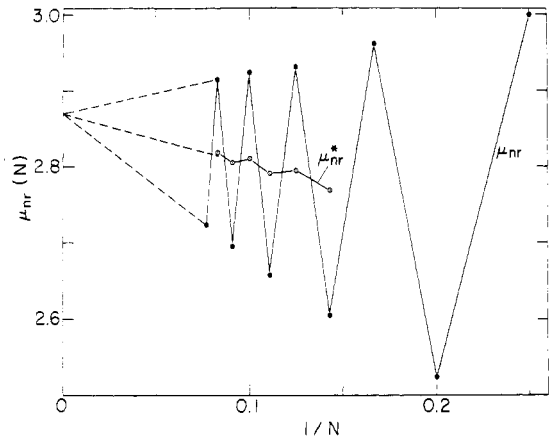

Figure 11. Plot of $\mu_{nr}(N)$ *vs.* $1/N$ for $\epsilon = 0$.

0.700, $\gamma_6 = 1.099$, $\gamma_8 = 0.887$, $\gamma_{10} = 1.176$, $\gamma_{12} = 1.036$. For $\gamma_N(\langle R^2_N\rangle_{rr})$, the sequence is: $\gamma_2 = 0.500$, $\gamma_4 = 1.704$, $\gamma_6 = 1.096$, $\gamma_8 = 1.386$, $\gamma_{10} = 1.255$, $\gamma_{12} = 1.308$. Both these sequences are converging very slowly preventing any estimation of their limit. The γ_N values are nevertheless consistent with a possible limiting exponent in the vicinity of 1.20. Figure 10 is a plot of $\langle S^2_N\rangle_{rr}/\langle R^2_N\rangle_{rr}$ *vs.* $1/N$ extrapolated to $1/N = 0$ for $\epsilon = 0$. With the limited data available a tentative limit of ~0.200 may be given for this ratio.

C. Critical Parameters. In the absence of a barrier Sykes[23] has shown that the number of open self-avoiding chains on a lattice is given by

$$C_N^{b} \simeq A_b N^{\alpha^b} \mu_b{}^N \text{ (bulk)} \quad N \to \infty \tag{14}$$

where A_b is a proportionality constant, μ_b is the limiting number of choices per step (see Hammersley[24]), and α^b is a critical index.

The presence of a solid barrier is not expected to alter the limiting behavior of C_N and the following representation for the number of self-avoiding walks initiated at a barrier which never returns to it, C_N^{nr}, may be written; namely

$$C_N^{nr} \simeq A_{nr} N^{\alpha^{nr}} \mu_{nr}{}^N \text{ (no return)} \quad N \to \infty \tag{15}$$

where the parameters have similar meanings as those defined in eq 14.

Likewise the number of self-avoiding walks which initiate on a barrier and randomly return to the barrier (loops) C_N^{rr} may be given by

$$C_N^{rr} \simeq A_{rr} N^{\alpha^{rr}} \mu_{rr}{}^N \text{ (random return)} \quad N \to \infty \tag{16}$$

and those self-avoiding chains C_N^{ar} which initiate on the barrier and return adjacent to the point of initialization by

$$C_N^{ar} \simeq A_{ar} N^{\alpha^{ar}} \mu_{ar}{}^N \text{ (adjacent return)} \quad N \to \infty \tag{17}$$

In this section estimates for α^{nr}, α^{rr}, and α^{ar} will be discussed. It would be constructive at this point to consider the behavior of these exponents for the case of the random walk. Here one finds[5-7]

$$\left.\begin{aligned} \alpha^b &= 0 \\ \alpha^{nr} &\simeq -1/2 \\ \alpha^{rr} &\simeq -3/2 \\ \alpha^{ar} &\simeq -5/2 \end{aligned}\right\} \text{ 3 dimensions} \tag{18}$$

Also $\mu = q$, where q is the coordination number of the lattice. Numerical studies[25] on self-avoiding walks have shown that: $\alpha^b \sim 1/6$ (3 dimensions). However to date no numerical study has investigated the behavior of α^{nr}, α^{rr}, and α^{ar} for self-avoiding walks. The effective coordination number $\mu_{nr}(\infty)$ is estimated by plotting $\mu_{nr}(N)$ *vs.* $1/N$, where

$$\mu_{nr}(N) = C_{N+1}{}^{nr}/C_N{}^{nr} \tag{19}$$

Extrapolation of the $\mu_{nr}(N)$ or averaged $\mu_{nr}(N)$ values, namely

$$\mu_{nr}{}^*(N) = (1/2)(\mu_{nr}(N) + \mu_{nr}(N)) \tag{20}$$

to $1/N = 0$ provides an estimate of $\mu_{nr}(\infty)$. Figure 11 is a plot of $\mu_{nr}(N)$ and $\mu_{nr}{}^*(N)$ *vs.* $1/N$. The effective coordination number is estimated to be 2.86. This value does not significantly differ from $\mu_b(\infty)$[26] and one may assume that

$$\mu_{nr}(\infty) \equiv \mu_b(\infty)$$

The critical index $\alpha^{nr}(\infty)$ was estimated indirectly by obtaining the surface contribution[27] to C_N^{nr}. One defines

$$\rho_N \equiv \frac{C_N{}^{nr}}{C_N{}^{b}} = \frac{A^{nr}}{A^b} N^{(\alpha^{nr}-\alpha^b)} [\mu_{nr}/\mu_b]^N \tag{21}$$

By forming the ratio

$$\frac{\rho_{N+1}}{\rho_N} \simeq \left[\frac{N+1}{N}\right]^{(\alpha^{nr}-\alpha^b)} \tag{22}$$

and expanding the right-hand side to order $1/N$ one obtains

$$\alpha_{nr}{}^0(N) \equiv (\alpha^{nr} - \alpha^b)_N \simeq N\left[\frac{\rho_{N+1}}{\rho_N} - 1\right] \tag{23}$$

Figure 12 is a plot of $\alpha_{nr}{}^0(N)$ *vs.* $1/N$ extrapolated to $1/N = 0$. A smooth curve is obtained by averaging the succes-

sive $\alpha_{nr}^{0}(N)$ values. $\alpha_{nr}^{0}(\infty)$ is estimated to be -0.480. With $\alpha^{b}(\infty) \simeq 1/6$, $\alpha^{nr}(\infty)$ is calculated to be ~ -0.32. This result is remarkably close to that conjectured by Silberberg.[3]

Estimation of the critical parameters for loops is much more difficult due to the limited amount of data available and only tentative assignments can be made. If one considers the probability for random loop formation P_N^{rr}, one may write that

$$P_N^{rr} \sim N^{-\beta_{rr}} \qquad N \to \infty \tag{24}$$

For a normal random walk $\beta_{rr} \simeq 3/2$. The effect of excluded volume is expected to decrease β_{rr} (see Appendix A) and this expectation is borne out. $\beta_{rr}(\infty)$ is estimated by using the method of Fisher.[28] Values of $\beta_{rr}(N)$ are given by

$$\beta_{rr}(N) = (N + 1)\left\{1 - \left[\frac{p_N^{rr}}{p_{N-2}^{rr}}\right]^{1/2}\right\} \tag{25}$$

$$\beta_{rr}'(N) = (N + 1)\left\{1 - \left[\frac{p_N^{rr}}{p_{N-2}^{rr}}\right]\right\} \tag{26}$$

where

$$P_N^{rr} \equiv C_N^{rr}/C_N^{nr} . \tag{27}$$

Oscillations found in the $\beta_{rr}(N)$ and $\beta_{rr}'(N)$ values are smoothed by forming

$$\begin{aligned} \beta_{rr}(N)^* &= (1/2)(\beta_{rr}(N) + \beta_{rr}(N + 2)) \\ \beta_{rr}'(N)^* &= (1/2)(\beta_{rr}'(N) + \beta_{rr}'(N + 2)) \end{aligned} \tag{28}$$

The following values were computed for $\beta_{rr}(N)^*$ and $\beta_{rr}'(N)^*$ for N = 6–12: $\beta_{rr}(6)^* = 1.37$, $\beta_{rr}'(6)^* = 1.24$, $\beta_{rr}(8)^* = 1.24$, $\beta_{rr}'(8)^* = 1.16$, $\beta_{rr}(10)^* = 1.28$, $\beta_{rr}'(10)^* = 1.21$, $\beta_{rr}(12)^* = 1.24$, $\beta_{rr}'(12)^* = 1.19$. The $\beta_{rr}(N)^*$ values seem to be tending to 1.26 and the $\beta_{rr}'(N)^*$ to 1.20. A tentative estimate for $\beta_{rr}(\infty)$ is taken as ~ 1.23. Since β_{rr} is given by

$$-\beta_{rr} \equiv \alpha^{rr} - \alpha^{nr} \tag{29}$$

one estimates $\alpha^{rr}(\infty) \simeq -1.56$. Considering the limited amount of loop data available, the agreement between the numerical estimate for α^{rr} and that given in Appendix A is quite remarkable (though perhaps fortuitous). It is also seen that α^{rr} is fairly insensitive to the excluded volume effect—this result is at first consideration unexpected. Poland and Sheraga[29] have considered the occurrence of a phase transition in nucleic acid models. In particular an abstract model was considered where the DNA structure was represented by two infinite chains made up of segments which can be bonded or nonbonded in a specific one-to-one fashion. The analogy between their abstract model of DNA and that of an infinite adsorbed chain at a surface is apparent. Here the completely ordered state occurs when all the segments are adsorbed. Desorption introduces loops with the surface. It was shown that whether or not a phase transition occurs in such a model depends on the parameter c in the generalized expression for the statistical weight of loops containing i units, namely

$$\ln w_i = ai - c \ln i - b \tag{30}$$

where if $c \leq 1$ no phase transition; $1 < c < 2$ higher order transition; $c \geq 2$ first-order transition; a and b being constants.

By comparing eq 30 with the logarithm of eq 16 one realizes that

$$\alpha^{rr} \equiv c \tag{31}$$

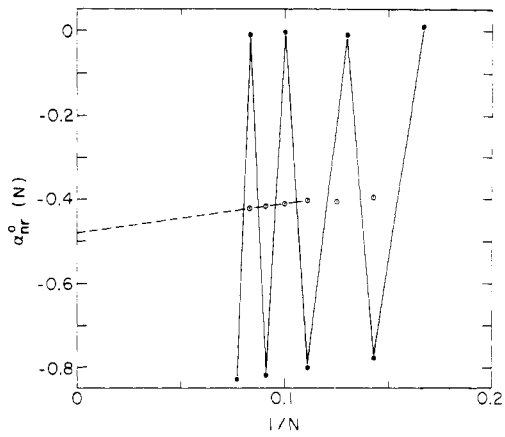

Figure 12. Plot of $\phi_{nr}^{0}(N)$ from eq 23 *vs.* $1/N$.

Fisher[28] has pointed out that for the normal random walk $c = d/2$ in d dimensions for loops returning to the origin in the absence of a barrier. Also Silberberg[3] has shown that critical desorption with the average length of loop regions approaching infinity requires that

$$1 < \alpha^{rr} < 2$$

It is found that excluded volume has little effect upon the phase transition characteristics of such a model, the order of the transition being greater than the first (*i.e.*, $\alpha^{rr} \simeq -1.56$). We do not report any estimate for α^{ar} since no reliable estimate for β_{ar} could be made.

Acknowledgment. The author expresses his deep appreciation to Professor J. Gillis of the Weizmann Institute of Science for his valuable advice on random walks and to Professor Cyril Domb of the University of London, King's College, for his suggestions on self-avoiding walk behavior. In addition the author acknowledges a postdoctoral fellowship from the Weizmann Institute of Science.

Appendix A[30]

The critical exponent α^{rr} in eq 16 can be estimated for a self-avoiding walk in the following manner.

Consider for a moment the random walk case. Let c_n be the number of random walks starting at a barrier and returning randomly to it after n steps (not necessarily for the first time). Let C_n be the number of random walks at the barrier after n steps for the first time. c_n and C_n are the coefficients of x^n in the generating functions

$$c(x) = \sum_{n=1}^{\infty} c_n x^n \tag{A-1}$$

and

$$C(x) = \sum_{n=1}^{\infty} C_n x^n \tag{A-2}$$

respectively. From renewal theory it can be shown that

$$C(x) = c(x)/[1 + c(x)] \tag{A-3}$$

Also in k dimensions it is known that

$$c_n \sim A(k)(2k)^n n^{-1/2} \qquad n \to \infty \tag{A-4}$$

where $A(k)$ is a constant. Equation A-1 becomes

$$c(x) = \sum_{n=1}^{\infty} A(k)(2k)^n n^{-1/2} x^n \tag{A-5}$$

after suitable expansion for large n, one finds

$$c(x) \sim (1 - (2k)x)^{-1/2} - 1 \qquad \text{(A-6)}$$

and

$$C(x) \simeq 1 - (1 - (2k)x)^{1/2} \qquad \text{(A-7)}$$

or

$$C_n \sim B(k)(2k)^n n^{-3/2} \qquad n \to \infty \qquad \text{(A-8)}$$

where $B(k)$ is a constant.

By an analogous argument c_n is now defined as the number of self-avoiding walks at the barrier after n steps and C_n the number of self-avoiding walks at the barrier for the first time after n steps. Equations A1–A3 are still applicable. It can be shown that

$$c_n \sim A' n^{(\alpha-\gamma/2)} \mu^n \qquad n \to \infty \qquad \text{(A-9)}$$

where A' is a constant, α is a long-range critical index solely dependent on dimensionality, γ the exponent in the expression for the mean-square end-to-end distance of a walk (*i.e.*, $\langle R^2_N \rangle = aN^\gamma$) and μ is the effective coordination number. Equation A-9 can be obtained from an empirical formula for the probability distribution of self-avoiding walks of size n. One finds that

$$c(x) = \sum_{n=1}^{\infty} A' \mu^n n^{(\alpha-\gamma/2)} \qquad \text{(A-10)}$$

which yields

$$c(x) \sim (1 - \mu x)^{\gamma/2-\alpha-1} - 1 \qquad \text{(A-11)}$$

and from relationship A-3

$$C(x) \sim 1 - (1 - \mu x)^{1+\alpha-\gamma/2} \qquad \text{(A-12)}$$

The final result is

$$C_n \sim B' n^{(\gamma/2-\alpha-2)} \mu^n \qquad n \to \infty \qquad \text{(A-13)}$$

In three dimensions numerical studies give the best estimates for γ and α as

$$\gamma \sim 6/5 \qquad (n \to \infty) \qquad \text{(A-14)}$$
$$\alpha \sim 1/6$$

therefore

$$C_n \sim B' n^{-1.57} \mu^n \qquad (n \to \infty) \qquad \text{(A-15)}$$

If

$$P_n^{rr} \equiv C_n^{rr}/C_n^{nr} \sim n^{-\beta_{rr}} \qquad \text{(A-16)}$$

one obtains

$$P_n^{rr} \sim n^{(-1.57-\alpha^{nr})} \qquad n \to \infty \qquad \text{(A-17)}$$

Empirically $\alpha^{nr} \sim -0.32$ so one stimates $\beta_{rr} \sim 1.25$.

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