the magnitude of α' approaches or exceeds that of $\tilde{V}$. The analysis leading to eq 5 also shows that calculations of the composition dependence of the partial molar volume based on simple equations of state such as the FOV and RK equations must be interpreted with particular caution where such equations predict sharp minima in $\bar{v}_2$, as they do for C_2–C_7 mixtures.

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(11) The expressions for the mixture properties $\tilde{T}$ and P^* in terms of those of the pure components should be viewed as relatively crude "mixing rules", adequate for the purpose. They are in general conformance with the corresponding states theory of Prigogine[5] and Patterson[6] and differ somewhat from the expressions proposed by Flory et al.[4] The expression for P^* is perhaps most open to question, but the partial molar volume is relatively insensitive to the "mixing rule" for P^*.
(12) We are not concerned here with any inconsistencies between the reference values recommended by these two sets of investigators because of the approximate nature of these calculations.

Surface Effects of the Four-Choice Cubic Lattice

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Recently, Mark and Windwer[2] and Lax[3-6] have investigated properties of self-avoiding chains generated in the presence of a barrier. One of us has shown[4-6] that the chain partition function for surface restricted walks can be represented by an equation of the following form

$$C_N^s \sim \mu_s N^{\alpha_s} \qquad N \to \infty \tag{1}$$

where C_N^s is the walk count in the presence of a barrier, α_s is the long-range index of surface chains, and μ_s is the effective coordination number. A similar expression exists for bulk generated chains,[7] namely,

$$C_N^b \sim \mu_b N^{\alpha_b} \qquad N \to \infty \tag{2}$$

where C_N^b is the walk count in the absence of a barrier, α_b is now the long-range index in bulk, and μ_b is the effective coordination number. The questions naturally arise: is α_s a dimensionally independent parameter as has been found for α_b; is μ_s identical in magnitude with μ_b or do they differ by some small number; what is the order of magnitude for the surface contribution to α_s defined as α^0? Lax,[4] in particular, estimated the magnitude of α^0, the difference between the value for the long-range index α_s of surface chains and that of the long-range index α_b of bulk generated chains. Estimates for α^0 are obtained by plotting $\alpha_N{}^0$ values from eq 3 vs. $1/N$ and extrapolating to $1/N = 0$

$$\alpha_N{}^0 \sim [N/(\mu_s/\mu_b)][\rho_{N+1}/\rho_N - \mu_s/\mu_b] \tag{3}$$

Table I
A List of the Number of Self-Avoiding Walks of Size N ($C_N{}^b$) in the Absence of a Solid Surface (Bulk Values) and the Number of Such Walks ($C_N{}^s$) (Surface Values) in the Presence of a Solid Barrier on the Four-Choice Cubic Lattice

N	$C_N{}^b$	$C_N{}^s$
4	360	192
5	1,368	692
6	4,992	2,388
7	18,408	8,324
8	67,320	28,936
9	247,152	101,704
10	900,552	356,600
11	3,290,328	1,257,044
12	11,965,752	4,420,548
13	43,588,848	15,595,912
14	158,264,544	54,980,576

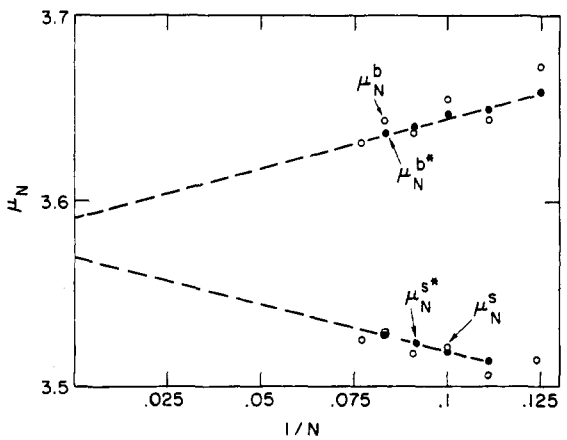

Figure 1. Plot of $\mu_N{}^s$ and $\mu_N{}^b$ and average values. $\mu_N{}^{s*} \equiv (\mu_N{}^s + \mu_{N+1}{}^s)/2$, $\mu_N{}^{b*} \equiv (\mu_N{}^b + \mu_{N+1}{}^b)/2$ vs. $1/N$.

$$\alpha_N{}^{0*} = (\alpha_N{}^0 + \alpha_{N+1}{}^0)/2 \tag{4}$$

where $\rho_N \equiv C_N{}^s/C_N{}^b$. (This equation is an expansion for ρ_{N+1}/ρ_N neglecting terms higher than N^{-1}.)

We now report results for the magnitudes of μ_s, μ_b, α^0, and α_s from an analysis of data obtained from self-avoiding walks generated on the four-choice cubic lattice in the presence and absence of a solid barrier. Table I lists the data for $C_N{}^s$ and $C_N{}^b$. The values obtained for $C_N{}^b$ agree with those computed from the ratio of $b_N/\langle d_N \rangle$ reported by Bellemans.[8]

Figure 1 is a plot of $C_{N+1}{}^s/C_N{}^s$ and $C_{N+1}{}^b/C_N{}^b$ vs. $1/N$. Extrapolating to $1/N = 0$ one obtains $\mu_b \sim 3.591$ and $\mu_s \sim 3.570$. These limiting estimates obtained from short walks differ by 0.02. Similar behavior was reported by Lax[3] for the diamond lattice. The question as to whether or not this difference persists for longer chains still remains to be clarified. If one assumes such differences are not significant (i.e., $\mu_b \equiv \mu_s$), one obtains the following values for $\alpha_N{}^{0*}$ from eq 3 and 4: $\alpha_8{}^{0*} = -0.3403$; $\alpha_9{}^{0*} = -0.3457$; $\alpha_{10}{}^{0*} = -0.3575$; $\alpha_{11}{}^{0*} = -0.3705$; $\alpha_{12}{}^{0*} = -0.3779$. Linear extrapolation of alternate pairs of $\alpha_N{}^{0*}$ values given above yield $\alpha_{9,11}{}^{0*} \to -0.480$ and $\alpha_{10,12}{}^{0*} \to -0.480$, respectively. This value is within the experimental error of that obtained for α^0 on the diamond lattice[4] and suggests that α^0 (as well as α_s) are long-range exponents which are solely dimensional dependent. Using the accepted value of $\alpha_b = \frac{1}{8}$ one estimates $\alpha_s \sim -0.313$.

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A Study of the Segmental Distribution of a Polymer Chain Terminally Attached to a Surface

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I. Introduction

Recently[1-3] attention has been focused on the behavior of a polymer chain terminally attached to a surface. A terminally attached chain is defined as one that is anchored to the surface at either one end (tail) or at both ends (loop). In particular Meier[3] and Hesselink[2] have obtained results using random walk statistics for the distribution of segments of tails and loops on the cubic lattice.

Such information is important in understanding the behavior of random walks near barriers, the stability of colloid dispersions, the size of the fold surface in polymer crystals, and the thickness of polymer films near weakly attracting interfaces. The effects caused by self-exclusion between chain elements have not been considered in either of these studies. Nevertheless it is apparent that such effects alter the relative location of polymer segments with respect to one another and hence may seriously alter the form of the distribution with respect to the surface.

In this paper we report a study of the distribution of segments for self-avoiding walks terminally attached to a surface generated on the diamond lattice by the method of exact enumeration.

II. Results and Discussion

The methods used to generate such walks are similar to those described previously.[1] In this particular study a count of the number of self-avoiding open walks (tails), i.e., those which do not return to the surface of size i, $C_{nr}(i,k,z)$ (where i is the number of segments $i-1$ being the number of bonds), having segment k in level z were obtained. In addition, the number of self-avoiding loops $C_{rr}(i,k,z)$, i.e., loops which return to the surface *randomly* for the *first time*, and the number of self-avoiding loops $C_{ar}(i,k,z)$, i.e., loops which return for the first time adjacent to their starting point, having segment k in level z were also obtained. These counts are reported in Tables I, II, and III, respectively. It should be noted that in Tables II and III only certain values of $C(i,k,z)$ are listed. The remaining values of $C(i,k,z)$ may be computed using the symmetry relationship.

$$C(i,k,z) \equiv C(i,i-k+1,z)$$

In addition all walk counts listed in Tables I–III are reduced by a factor of 2 due to symmetry considerations.

(1) **Walk Probabilities.** One defines the conditional probability for finding a walk of size i with segment k in level z and its first segment in level zero by

$$P_{nr}(i,k,z) \equiv C_{nr}(i,k,z)/C_{nr}^{S} \quad (1)$$

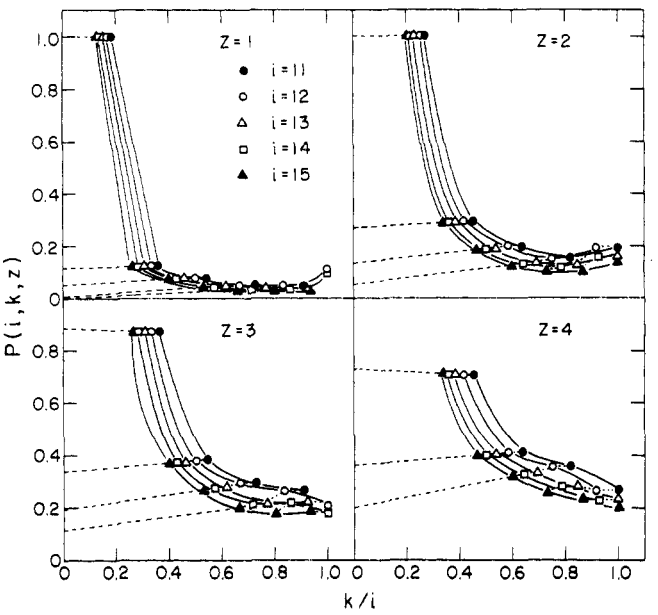

Figure 1. Plots of probability $P_{nr}(i,k,z)$ vs. k/i.

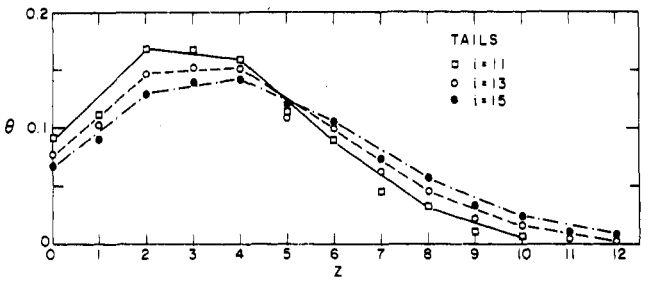

Figure 2. Plots of fraction of segments vs. normal to the surface distance for tails.

where C_{nr}^{S} is the total number of self-avoiding tails obtained. These probabilities are normalized so that

$$\sum_{z=0}^{z=i-1} P_{nr}(i,k,z) = 1 \quad (2)$$

and also

$$\sum_{z=0}^{z=i-1} \sum_{k=1}^{k=i} \rho_{nr}(i,k,z) = 1 \quad (3)$$

where

$$\rho_{nr}(i,k,z) \equiv P_{nr}(i,k,z)/i \quad (4)$$

It is apparent that $P_{nr}(i,k,z)$ can also be looked upon as the average number of kth segments per chain located in level z, whereas $P_{nr}(i,k,z)/i$ represents the fraction of kth segments in level z. In addition one may compute the average number of segments per chain, $i\theta(i,z)$, where $\theta(i,z)$ is the fraction of segments in any level, by summing the $P_{nr}(i,k,z)$ over k, i.e.,

$$i\theta(i,z) = \sum_{k=1}^{k=i} P_{nr}(i,k,z)$$

Figure 1 is a normalized plot of $P_{nr}(i,k,z)$ vs. k/i for various z levels. By connecting points corresponding to the same value of k one obtains curves of constant k, and extrapolating to $k/i = 0$ one obtains an estimate for $P_{nr}(\infty,k,z)$. It is seen that for most values of k straight lines are obtained; only for large k/i does curvature appear due