The function $K_f(\rho;N)$ which is defined in eq 6 and 7 also appears in the work of Casassa and Tagami[16] (their eq 4). These authors have obtained the following value of $K_f(\rho;N)$ in the vicinity of $\rho = \infty$ (their eq 13 which is corrected in footnote 18 of Casassa[17]),

$$K_f(\rho;N) \sim 1 - 2\psi(f)(fN/6\rho^2)^{1/2} + O(N/6\rho^2) \quad (18)$$

where

$$\psi(f) = \left(\frac{f}{\pi}\right)^{1/2} \int_0^\infty [\mathrm{erf}(t^{1/2})]^{f-1} e^{-t}\, dt \quad (19)$$

Inserting (18) in (17), the following formula proposed by Casassa[17] for the average value of the span is obtained,

$$\langle R \rangle = 2(2Nf/3)^{1/2}\psi(f) \quad (20)$$

It is readily verified by combining (18) and (15) that the span distribution is properly normalized, i.e., the zeroth moment is equal to unity. Finally, we remark that it is possible in principle to obtain higher order correction terms to the expression for $K_f(\rho;N)$ of Casassa and Tagami[16] which is reproduced in eq 18. For each additional correction term, it will be possible to calculate an additional moment of the span pdf from eq 15.

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Monte Carlo Study of a Self-Interacting Polymer Chain

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ABSTRACT: A Monte Carlo study of the Domb–Joyce Model of a polymer chain was made by simulating random walks on the simple cubic lattice. It is shown that the recent formula advanced by Domb and Barrett for the expansion factor α^2 as a function of an intramolecular potential (for weak perturbations) is in excellent agreement with the computer simulations. The behavior of the partition function for such a model is also investigated.

An important problem in polymer physics is the configurational characteristics of long flexible chains in dilute solution. Early models of such systems treated the chain as a normal random walk (NRW). This model is primitive since it neglects self-exclusions in the chain. To account for such "excluded volume" effects a self-avoiding walk (SAW) model of the polymer chain must be studied. The self-avoiding walk model mathematically is a non-Markovian process and very complicated. Nevertheless, by application of both analytic and numerical techniques[2-4] some conclusions concerning the behavior of configurational properties of both NRW and SAW models have been advanced. In particular, it has been found that for models studied in three dimensions the mean-square end-to-end distance, $\langle R_N^2 \rangle$, of such chains obeys the following simple asymptotic formulas

$$\langle R_N^2 \rangle_0 = AN \qquad \text{(NRW)} \quad (1)$$

$$\langle R_N^2 \rangle \sim AN^{1.20} \qquad \text{(SAW)} \quad (2)$$

where A is a model dependent constant and the exponent is only dimensionally dependent or universal. Equation 2 has been found to be strictly true for ordinary SAW walks simulated on three-dimensional lattices. Domb[5] advanced the hypothesis that the exponent in eq 2 is a universal parameter of polymer systems and should therefore be insensitive to models studied in a given dimension. This idea is supported by the studies of Hioe[6] and Watson.[7] The general form of eq 2 is retained for models considering finite intramolecular interactions[8,9] and varying excluded volume,[10-16] but in general the exponent appears to be a function of the intermolecular potential and excluded volume effects. Moreover, the connection between the simple form of eq 2 and the many formulas advanced for the expansion factor of the end-to-end distance α^2 where,

$$\alpha_N^2 = \langle R_N^2 \rangle / \langle R_N^2 \rangle_0 \quad (3)$$

is not straightforward. Thus a fundamental problem remaining is an understanding of the behavior of the self-interacting chain.

Recently Domb and Joyce[17] have specified a lattice version of the expansion factor problem. They have shown that α^2 may be expressed as a perturbation series in the interaction parameter ω of the form;

$$\alpha^2 = 1 + \sum_i K_i \omega^i \quad (4)$$

where the K_i's are functions of $N^{i/2}$. Here $\omega = 0$ corresponds to the NRW and $\omega = -1$ to the SAW. They note that the continuum model may also be expressed as a power series in

Table I
A list of $\langle R_N^2(v) \rangle$ for Various Chain Lengths

v/N	10	20	30	40	50	60	70
0.5	13.3255	29.7701	48.0197	66.6875	87.2929	108.606	126.409
0.6	12.6999	27.9894	44.7761	61.9416	80.5480	101.199	117.925
0.65	12.3898	27.0909	43.1500	59.5799	77.3598	96.9675	113.308
0.7	12.0805	26.1811	41.4690	57.1927	74.1468	92.5356	108.461
0.75	11.7713	25.2551	39.8182	54.7494	70.8331	87.9453	103.362
0.8	11.4614	24.3072	38.0821	52.2154	67.3538	83.1838	97.9553
0.85	11.1502	23.3302	36.2747	49.5487	63.6436	78.1881	92.1490
0.87	11.0251	22.9294	35.5266	48.4336	62.0776	76.1003	89.6885
0.90	10.8369	22.3154	34.3715	46.6960	59.6212	72.8419	85.7855
0.91	10.7739	22.1070	33.9766	46.0970	58.7697	71.7155	84.4244
0.92	10.7109	21.8964	33.5761	45.4869	57.8998	70.5658	83.0273
0.93	10.6477	21.6837	33.1697	44.8649	57.0100	69.3904	81.5906
0.94	10.5843	21.4687	32.7569	44.2300	56.0987	68.1866	80.1100
0.95	10.5209	21.2512	32.3374	43.5811	55.1640	66.9513	78.5805
0.96	10.4573	21.0311	31.9106	42.9171	54.2036	65.6809	76.9963
0.97	10.3936	20.8053	31.4760	42.2365	53.2149	64.3711	75.3504
0.98	10.3298	20.5825	31.0329	41.5379	52.1947	63.0164	73.6345
0.985	10.2978	20.4685	30.8080	41.1812	51.6716	62.3203	72.7472
0.99	10.2658	20.3537	30.5807	40.8193	51.1391	61.6104	71.8383
0.992	10.2529	20.3075	30.4891	40.6730	50.9234	61.3224	71.4683
0.995	10.2337	20.2380	30.3509	40.4518	50.5966	60.8857	70.9061
0.997	10.2209	20.1915	30.2583	40.3022	50.3767	60.5913	70.5263
1.0	10.2016	20.1215	30.1186	40.0784	50.0433	60.1447	69.9487

the interaction parameter and show that the functional form for α^2 is identical for both lattice and continuum models. This is the first comprehensive supportive evidence for the universality hypothesis advanced by Domb[5] in 1963. Domb and Barrett[18] computed the virial coefficients in eq 4 to the third order and present a universal function ψ for the expansion parameter.

$$\psi^{15} = [1 + 10z + (70\pi/9 + 10/3)z^2 + 8\pi^{3/2}z^3]^2$$
$$z = (3/2\pi)^{3/2}N^{1/2}\phi \qquad (5)$$

The function should be rigorously correct in the limit of large chains, small excluded volume. To extend the range of ψ for large excluded volume exact enumeration studies on the Domb–Joyce model were made and preliminary results reported by Domb, Barrett, and Lax.[19] More comprehensive results of these studies are now being published. In this paper we report a Monte Carlo study of contacts in random walks on the simple cubic lattice as a model of a self-interacting polymer chain and proceed to investigate the validity of eq 5 for small excluded volume. We also investigate other generalized properties of the Domb–Joyce model in the vicinity of small perturbations near the random walk case.

Method

An unenriched Monte Carlo generation of random walks on the simple cubic lattice was performed. A short-range interaction parameter v was associated with each self-intersection of the chain. For a configuration with k contacts the total chain energy is therefore v^k. This corresponds to the generalized Domb–Joyce model of a random chain on a lattice with an intramolecular interaction $-\omega\delta_{ij}$ between any pair of points in the configuration, i and j being the sites occupied by the ith and jth elements of the walk and δ_{ij} is the delta function. Thus only elements occupying the same site contribute to the total energy of the chain. A partition function for the system is formed in the following manner;

$$Q_N = \sum_k C_{N,k} v^k \qquad (6)$$

where $C_{N,k}$ is the number of random walks of size N having k contacts (no returns to the origin). Averaged configurational properties are computed by;

$$\langle R_N^2(v) \rangle = \sum_k r_{N,k}^2 C_{N,k} v^k / Q_N \qquad (7)$$

where $r_{N,k}^2$ is the value of the end-to-end distance for chains of size N and k contacts. Listings were made of the $r_{N,k}^2$ and $C_{N,k}$ for samples of 100 000 configurations for each chain length. Random walks of lengths up to 70 steps were generated. It should be noted that the interaction potential v in eq 6 and 7 is related to the ω in the Domb–Joyce notation by,

$$v = (1 + \omega) \qquad (8)$$

i.e., $v = 1$, $\omega = 0$ corresponds to the random walk case and $v = 0$, $\omega = -1$ corresponds to the self-avoiding walk case. It is thus possible to investigate the smooth transition from random walk → self-avoiding walk behavior by variation of v from $1 \rightarrow 0$.

Results and Discussion

(A) End-to-End Distance, $\langle R_N^2 \rangle$. In Table I we list the average end-to-end distance $\langle R_N^2(v) \rangle$ for random walks of sizes $N = 10$ to 70 steps as a function of v. Wall, Windwer, and Gans,[8] Mazur and McCrackin,[9] and Smith and Fleming[11] investigated self-avoiding walk models with finite intramolecular interactions on various lattices and they showed the mean-square end-to-end distance obeys

$$\langle R_N^2 \rangle \sim A(\phi)N^{\gamma(\phi)} \qquad (9)$$

where ϕ is the interaction parameter. The first test of the data is to check the fit of the end-to-end distance to eq 9. Figure 1 is a plot of $\log \langle R_N^2(v) \rangle$ vs. $\log N$ for $v = 0.5$–1.0. We obtain smooth curves through all points. A least-squares fit of the data yielded the exponents listed in Table II. It is seen that eq 9 describes the data; however, the error in the exponent obtained is sufficient to keep $\gamma(v)$ fairly constant for all v except in the vicinity of 1. If one keeps in mind the finite lengths of the walks involved and the possibility of extremely slow convergence near $v = 1$, then one cannot rule out the ideas advanced by Domb[2a] as to the universality of γ.

A modification to the extrapolation formulas normally used

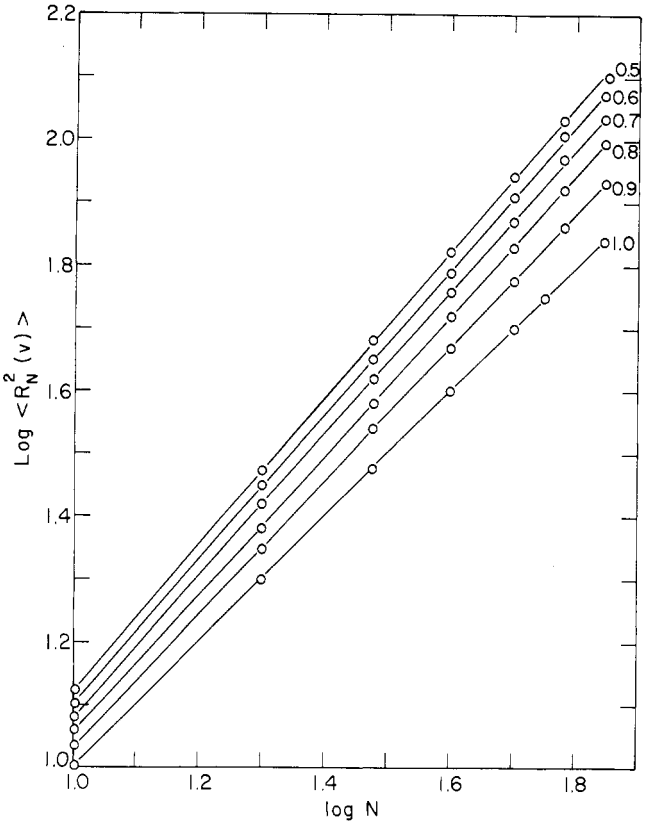

Figure 1. Plots of log $R_N^2(v)$ vs. log N.

Table II
A List of the Exponent $\gamma(v)$ (eq 9) as a Function of v (Values were obtained from Least-Squares Fit of $\langle R_N^2 \rangle$ Data)

v	$\gamma(v)$	v	$\gamma(v)$
0.5	1.16 ± 0.01	0.8	1.11 ± 0.01
0.6	1.15 ± 0.01	0.9	1.07 ± 0.01
0.7	1.13 ± 0.01	1.0	0.99 ± 0.003

for α^2 assumes a Darboux form,[19] namely,

$$\alpha^2(v) = N^{1/5}(A(v) + B(v)/N) \tag{10}$$

or

$$\langle R_N^2(v)\rangle \sim A(v)N^{6/5} + B(v)N^{1/5} \tag{11}$$

This modification expresses α^2 as a two-parameter function and plots of $\alpha^2(v)/N^{1/5}$ *vs.* $1/N$ or $\langle R_N^2(v)\rangle/N^{6/5}$ vs. $1/N$ should be linear with slope $B(v)$ intercept $A(v)$. Figure 2 is a plot of $\langle R_N^2(v)\rangle/N^{6/5}$ vs. $1/N$. It is seen that the assumption is approximately obeyed for $0.5 \leq v < 1, N \geq 40$ with scatter increasing with increasing excluded volume. One cannot expect the data to be indicative of true behavior for large excluded volume, since the sampling of configurations with few contacts is poor. Also the finite size of the chains generated precludes a valid test in regions where convergence may be slow (near $v = 1$). We find that in the intermediate range the approximation is not too bad.

(B) Expansion Factor, α^2. Figure 3 is a plot of $\alpha_N^2(v)$ vs. v for finite chains. In general if the two parameter assumptions given in eq 10 were strictly correct, curves of constant $\eta = [-N^{1/2}\omega]$ should be horizontal. It is seen that such curves are fairly linear but not horizontal; it is clear that higher order terms are necessary to describe the behavior in this region.

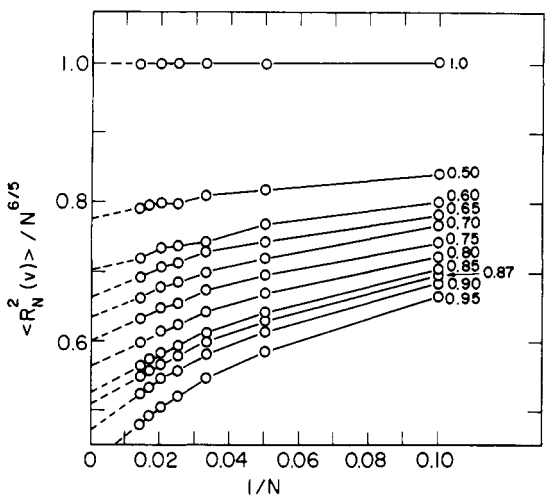

Figure 2. Plots of $\langle R_N^2(v)\rangle/N^{6/5}$ vs. $1/N$, except for $v = 1$ where $\langle R_N^2(1)\rangle/N$ vs. $1/N$ is shown.

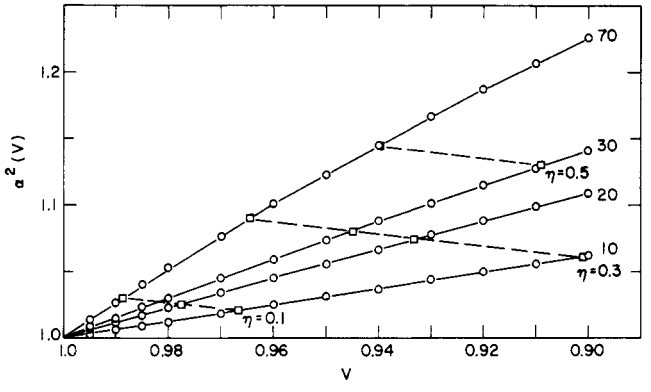

Figure 3. Expansion factor $\alpha_N^2(v)$ vs. v.

The expansion factor α^2 may be expressed in terms of the parameter η $(=-N^{1/2}\omega)$. Barrett[20] gives the following relationship for $\alpha^2(\eta)$ to order three.

$$\alpha^2(\eta) = [1 + 5f_0/(\pi)^{1/2}\eta + (35/18 + 5/6\pi)f_0^2\eta^2 + f_0^3\eta^3]^{2/15} \tag{12}$$

here f_0 is a lattice-dependent constant given for the SC lattice by:

$$f_0 = -2\pi^{1/2}(3/2\pi)^{3/2} \tag{13}$$

$((f_0\eta/2\pi^{1/2})$ is the standard excluded volume parameter used in expansion factor theories). This expression is analogus to the one presented by Domb and Barrett.[18] It is a simple matter to check the validity of eq 12.[23] One simply constructs curves of $\alpha_N^2(\eta)$ vs. η and extrapolates the $\alpha_N^2(\eta)$ vs. $N^{-1/2}$ to obtain an asymptotic estimate for $\alpha_\infty^2(\eta)$. Table III lists $\langle R_N^2(\eta)\rangle$ for η in the range 0–3. In Figure 4 we show plots of $\alpha_N^2(\eta)$ vs. η for $N = 10, 20, 40, 60$ together with an estimated curve obtained by extrapolation of the $\alpha_N^2(\eta)$ data vs. $N^{-1/2}$ for constant η. Curves of $\alpha_N^2(\eta)$ vs. $N^{-1/2}$ are shown in Figure 5. A least-squares fit yielded the estimates shown in Figure 4 (curve labeled "this study").

Also shown in Figure 4 are values calculated from eq 12 (curve DB). It is seen that agreement to within 3% is obtained for the range $\eta = 0 \rightarrow 1$. We consider this to be within acceptable error limits for the extrapolations and suggest that eq 12 is a valid representation of the behavior of α^2 near $v = 1$ $(\omega = 0)$. The universitality of eq 12 must still be tested by Monte Carlo studies on other lattices.

Table III
A List of $\langle R_N^2(\eta) \rangle$ for Finite Chains

η/N	10	20	30	40	50	60	70
0.1	10.4064	20.6279	30.9432	41.2530	51.5659	62.0381	72.2045
0.2	10.6034	21.1415	31.7811	42.3740	53.0135	63.8349	74.3299
0.3	10.8054	21.6195	32.5481	43.3835	54.3978	65.5518	76.3458
0.4	11.0001	22.0860	33.2922	44.4219	55.8208	67.2011	78.2682
0.5	11.2001	22.5630	34.0163	45.4253	57.0999	68.7922	80.1100
0.7	11.5917	23.4690	35.4509	47.3429	59.5368	71.7155	85.5907
1.0	12.1795	26.4738	37.4766	49.9863	62.9454	75.9943	88.4119
1.5	13.1619	26.8194	40.6320	54.1009	68.1367	82.5985	95.5726
2.0	14.1718	28.8277	43.6395	57.9611	73.0348	88.6903	102.201
3.0	16.3926	32.8464	49.5998	65.4444	82.0975	100.123	114.156

Table IV
A List of the Number of Open Walks (no Returns to the Origin), $C_N(v)$, for Chains of Lengths 10–70

v/N	10	20	30	40	50	60	70
0.5	36062.6	9481.23	2373.72	591.766	143.449	35.6829	8.60730
0.6	43515.9	14386.4	4542.30	1425.98	435.048	134.616	41.3896
0.7	52741.5	22218.3	8974.26	3591.91	1402.54	551.548	216.854
0.8	64303.7	35163.7	18535.3	9650.99	4933.74	2533.05	1295.68
0.85	71200.5	44776.1	27243.0	16363.6	9683.95	5751.25	3394.56
0.9	79009.1	57604.2	40833.6	28598.8	19806.7	13753.8	9478.37
0.92	92422.8	63925.9	48326.2	36127.8	26749.7	19848.7	14617.6
0.95	87890.6	75043.3	62741.6	51989.2	42780.4	35245.8	28856.0
0.97	91786.2	83766.3	75144.2	66959.8	59377.3	52680.1	46530.4
1.0	98042.0	99308.0	99605.0	99749.0	99819.0	99836.0	99896.0

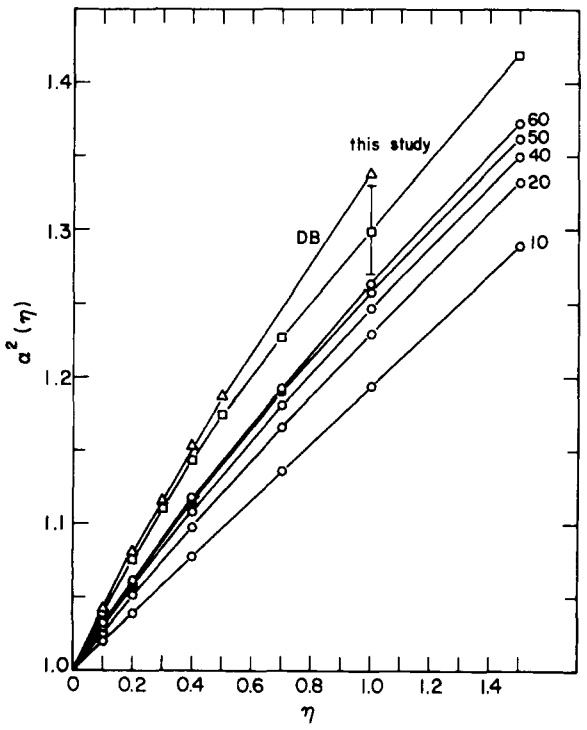

Figure 4. Expansion factor $\alpha_N^2(\eta)$ for finite chains of size N vs. η ($=-N^{1/2}\omega$), and curves for $\alpha_N^2(\eta)$ from eq 12 and extrapolations of α_N^2 data.

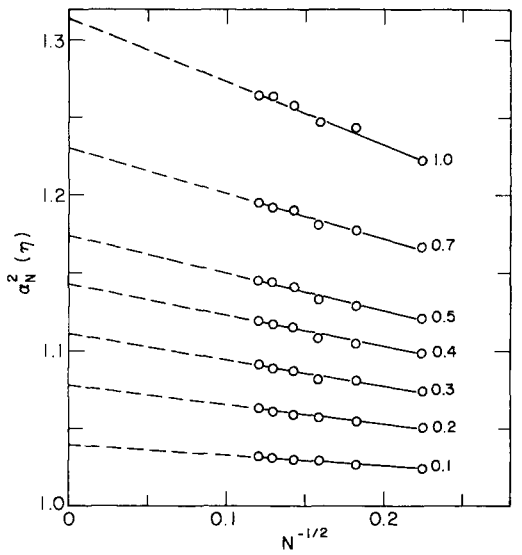

Figure 5. Curves of $\alpha_N^2(\eta)$ vs. $N^{-1/2}$.

(C) Chain Partition Function. Table IV lists $C_N(v)$, the number of chains obtained as a function of v for chains of lengths $N = 10 \rightarrow 70$. For each chain length ensemble of 100 000 random walks were generated. (The value for $v = 1$ does not equal 100 000 for any chain length since the number of returns to the origin was listed separately.) The partition function for SAW's is given for large N by:[21]

$$C_N \sim AN^{\alpha}\mu^N \tag{14}$$

where A is a model dependent constant. α has been shown from exact enumerations to be lattice independent in a given dimension, the best estimate to date being $\frac{1}{6}$ in three dimensions, and μ is the effective coordination number. If an intramolecular potential is present one rewrites eq 14[9]

$$C_N(v) \sim A(v)N^{\alpha}\mu(v)^N \tag{15}$$

here we assume α is independent of v in the region $0 \leq v < 1$. This approach differs from previous treatments[8,9] of the behavior of the partition function with interactions; however,

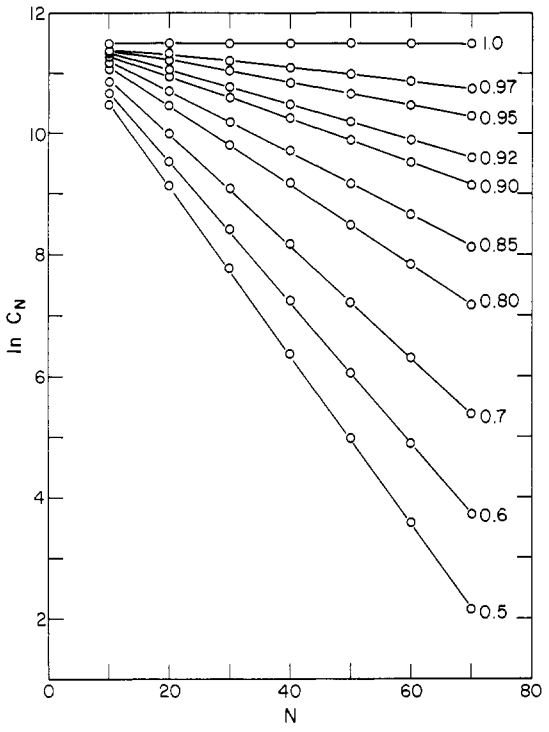

Figure 6. Plots of ln $C_N(\upsilon)$ vs. N.

Table V
A List of the Attrition Constant, $\lambda(\upsilon)$, and the Effective Coordination Number, $\mu(\upsilon)$, as a Function of υ

υ	$\lambda(\upsilon)$	$\mu(\upsilon)$
0.50	0.8700 ± 0.005	5.220
0.60	0.8898 ± 0.004	5.338
0.70	0.9122 ± 0.001	5.473
0.80	0.9367 ± 0.001	5.620
0.85	0.9503 ± 0.001	5.702
0.90	0.9651 ± 0.0004	5.791
0.92	0.9714 ± 0.0004	5.829
0.95	0.9815 ± 0.0003	5.889
0.97	0.9886 ± 0.001	5.932

we will shortly show that the assumption is reasonable. We introduce one more assumption, namely,

$$C_N(\upsilon) = A(\upsilon)N^{\alpha}\mu(\upsilon)^N + B(\upsilon)N^{\alpha-1}\mu(\upsilon)^N \quad (16)$$

where $B(\upsilon)$ is a constant.

A result from Monte Carlo studies on self-avoiding walks is the familiar attrition equation,[2b]

$$C_N = C_0 \exp(-\lambda N) \quad (17)$$

where λ is the attrition constant. We assumed that eq 17 is applicable in the following form,

$$C_N(\upsilon) = C_0(\upsilon) \exp(-\lambda(\upsilon)N) \quad (18)$$

Figure 6 is a plot of ln $C_N(\upsilon)$ vs. N. It is seen that eq 18 is justified by the nice straight lines obtained. Least-squares fit of the data yielded the best estimates for the slope λ which are reported in Table V. Also listed in Table V are values for $\mu(\upsilon)$ computed from,

$$\mu(\upsilon) = \sigma \exp(\lambda(\upsilon)) \quad (19)$$

where $\sigma = 6$, the coordination number of the SC lattice. We note the agreement for $\mu(0.5) = 5.22$ obtained in this study

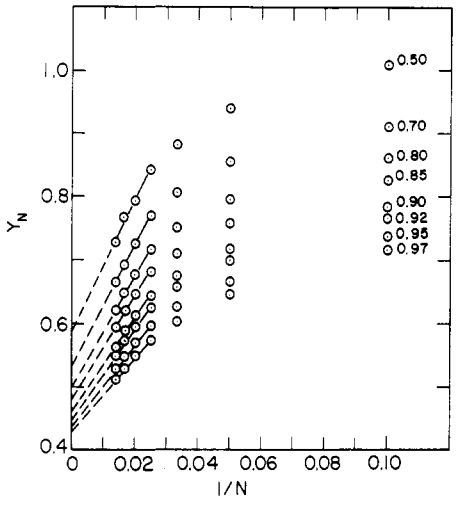

Figure 7. Curves of $Y_N(\upsilon)$ (eq 21) vs. $1/N$.

Table VI
A List of the Estimates for the Amplitude, $A(\upsilon)$ (eq 20)

υ	$A(\upsilon)$	υ	$A(\upsilon)$
0.5	0.590	0.9	0.450
0.7	0.535	0.92	0.445
0.8	0.500	0.95	0.435
0.85	0.480	0.97	0.425

with the value obtained from exact enumerations of short chains ($N \leq 10$) on the same lattice model of $\mu(0.5) = 5.19$.

It is more convenient in Monte Carlo studies to treat the reduced partition function namely,

$$Y_N'(\upsilon) = C_N(\upsilon)/C_N(1) = A(\upsilon)N^{\alpha}(\mu(\upsilon)/\sigma)^N + B(\upsilon)N^{\alpha-1}(\mu(\upsilon)/\sigma)^N \quad (20)$$

We form

$$Y_N(\upsilon) = Y_N'(\upsilon)/[\mu(\upsilon)/\sigma]^N N^{\alpha} = A(\upsilon) + B(\upsilon)N^{-1} \quad (21)$$

and show that plots of $Y_N(\upsilon)$ vs. $1/N$ are reasonably linear and justify eq 16. Figure 7 is such a plot for selected values of υ. Table VI lists the estimates of $A(\upsilon)$ obtained.

Conclusions

It is noted that the results presented here cannot properly be extrapolated to small values of υ. The statistical validity of the data can only be trusted in the region near $\upsilon = 1$. Nevertheless, while the results presented are limited to short chains, and sampling of configuration with few contacts is poor, it is interesting to note the agreement between $\alpha^2(\eta)$ vs. η for $\eta \leq 1$ obtained and that suggested by Domb and Barrett.[18] In light of the independent study by Alexandrowicz and Accad[15] and the recent report by Barrett[22] of agreement between the behavior of α^2 (as suggested by Domb et al.[17,18]) and computer simulations, we suggest that further attention be paid to investigating the universality of such ideas.

References and Notes

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Monte Carlo Calculations on Polypeptide Chains. 10. A Study of the Kinetics of the Helix–Coil Transition

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ABSTRACT: A stochastic model of the kinetics of the helix–coil transition based on the equilibrium statistical mechanical theory of Lifson and Roig is presented. A Monte Carlo simulation of the kinetics based on the stochastic model was used to study the kinetics of the helix–coil transition. Kinetics simulations were conducted from several initial values of the fractional hydrogen bonding parameter θ to each equilibrium value of θ. A spectrum of relaxation times and characteristic weighting constants is reported for each kinetics simulation. The chain lengths used in this study were 15, 34, and 85 residues. It was found that at each chain length the relaxation times depend only on the equilibrium value of θ while the characteristic weighting constants depend on both the initial and equilibrium values of θ. The mean relaxation time was calculated for several relaxations at chain lengths 15, 34, and 85. It was found that the mean relaxation time does not reflect the correct order of magnitude of the slowest relaxation process. In addition, it was found that pure random coil species do not survive long enough to be measured by nmr spectroscopy and therefore values of $\tau \geq 10^{-1}$ s do not reflect a relaxation time of the helix–coil transition.

I. Introduction

Rapid advancements have been made in treating macromolecular chain conformations by equilibrium statistical mechanics.[1-3] This progress has been due in large measure to the adoption of Volkenstein's rotational isomeric state approximation[1] which allowed the mathematical formalism of the Ising lattice model to be applied to this important area of research. Recent improvement in the mathematical formalism, developed by Flory and his co-workers[3] using improved matrix methods, has resulted in a very elegant and practical mathematical formulation which has found widespread use. These methods have been applied prolifically to biopolymers, especially to the helix–coil transition in polypeptides and nucleic acids.[4]

Unlike the situation for the equilibrium theory, the rate theory of macromolecular conformational changes is not well developed. There are several theories of the kinetics of the helix–coil transition in polypeptides, however, they are either limited to treatment of only the initial rate[5-7] or to perturbations from equilibrium so large that the reverse reaction is negligible.[8] The initial rate treatment has been widely used to interpret experimental kinetics data obtained using such physical techniques as temperature jump, ultrasonic absorption, and dielectric relaxation. Using these techniques, relaxation times of the order of magnitude of 10^{-5}–10^{-8} s have been reported. Nuclear magnetic resonance spectroscopy has been used to study the helix–coil transition under equilibrium conditions.[9,10] Lifetimes of peaks in the NMR spectra, which have been attributed to the helix and random coil, are reported to be greater than 10^{-1} s.[9] Several workers[11,12] have investigated this apparent contradiction in relaxation times and have attempted to show that the slow relaxation time is due to polydispersity. For example, Bradbury et al.[22] compared fractionated and unfractionated samples using NMR and ORD. These authors concluded that it was highly likely that the α-CH doublet appearing in NMR spectra is due to polydisperse samples. However, considerable controversy remains concerning the nature of the slow relaxation time obtained using NMR spectroscopy.

In this paper we present a stochastic model of the kinetics of the helix–coil transition based on the equilibrium statistical mechanical theory of Lifson and Roig.[13] Using this model, we introduce a Monte Carlo method of simulating the relaxation from an initial value of the fractional helix content θ to an equilibrium value of θ. The equilibrium sample generated in this manner was used previously to study the effect of excluded volume on the helix–coil transition.[14] The chain lengths studied in this paper are 15, 34, and 85 monomers in length. A spectrum of normal modes of relaxation with characteristic amplitudes is reported for all three chain lengths using several initial and equilibrium values of θ. The mean relaxation time will be calculated for several relaxations in order to relate the Monte Carlo results to experimental data. In addition, it will be shown that a slow relaxation time of 10^{-1} s is inconsistent with the survival time of the pure random coil.

II. Models and Methods

In the theory of the helix–coil transition, Lifson and Roig[13] defined the statistical weight parameters u, v, and w as configuration integrals over φ–ψ space, u over the values of φ and ψ in the coil region of a single unit, v over the helical region of such a unit, and w over three consecutive helical units. A polypeptide chain in a given conformation can then be divided into alternating sequences of coil states with statistical weight