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STATISTICAL MECHANICS OF POLYMER SYSTEMS

PROGRESS REPORT
1990-91

by

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GENERAL INTRODUCTION

In the past year we have concentrated our efforts in the computer simulation of polymer dynamics. Several areas have been studied. First, we have continued our work on chains in the theta region and have completed a detailed study of the lifetime of nearest neighbor pair contacts in an effort to understand the slowing of the shorter range motions of the chain observed by Downey and Kovac. This work has been submitted to *Macromolecules* and the text of that manuscript has been included as a part of this report.

Second, we have continued study the dynamics of chains tethered to rigid interfaces. Professor Karl Freed of the University of Chicago asked us to study a chain in a reflecting wedge and compare the simulation results to his RG calculations. This work has been completed and the comparisons are quite satisfactory. A copy of the manuscript reporting that work is also included as part of this report.

Third, we have extended our work on shape relaxation in star polymers to look at the effects of a bath of linear molecules on the shape and shape relaxation of a star polymer. This work is nearly complete and should be ready for submission to a journal in a few months.

Seminars on our work on dynamics near the theta point have been presented at four different colleges and universities during the past year.

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Submitted to Macromolecules

The Role of Attractive Forces in the Dynamics
of Polymer Chains Near the Theta Point

by

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ABSTRACT

The role of attractive forces in the dynamics of lattice model chains near the theta point has been investigated using a Monte Carlo method. The mean square internal chain distances of the first four normal modes have been computed to investigate the effects of local chain expansion on the dynamics. The distribution of lifetimes of pair contacts between non-adjacent chain segments has also been determined. We find that the observed distribution of pair contact lifetimes provides a possible explanation for the slowing of the motions of the third Rouse mode found recently by Downey and Kovac. These results are qualitatively consistent with the physical mechanism responsible for the "gel modes" introduced by Brochard and DeGennes. The simulation results also provide an alternative explanation of some recent experimental results concerning the relaxation of anthracene labelled polyisoprene chains.

INTRODUCTION

In two recent publications Downey and Kovac studied the dynamics of lattice models of polymer chains in the theta region and below using a Monte Carlo method.¹ In the Downey-Kovac model the excluded volume condition was rigorously maintained and the chains were brought to the theta condition by the addition of an attractive nearest neighbor interaction between adjacent non-bonded chain segments. The detailed dynamics of these model chains were studied by calculating the autocorrelation functions of the first three Rouse coordinates, which were found to be good normal coordinates. The relaxation times, τ_k , of these normal modes were studied as a function of attractive energy, chain length and mode number. The remarkable result of this work was that the scaling exponents characterizing the chain length dependence of the relaxation times of the various normal modes, α_k , defined by the relation

$$\tau_k \sim (N-1)^{\alpha_k} \quad (1)$$

showed quite different behavior as a function of the attractive interaction $\phi = -\epsilon/kT$. While the exponent characterizing the longest Rouse time, α_1 , showed the expected behavior, decreasing from 2.2 in the excluded volume region to 2.0 in the theta region, the exponent characterizing the shortest mode studied, α_3 , decreased much more slowly as the theta point was approached from above, never becoming as small as 2.0. In the collapse region below the theta point α_3 increased to values well above 2.2 while α_1 continued to decrease. Physically, this indicates that the third mode is relaxing much more slowly in the theta

region and below than would be predicted by ideal Rouse behavior.

Three possible explanations for this behavior were proposed by Downey and Kovac. The first possibility is that the increasing segment density in the theta region is causing the exponent α_3 to increase. Previous results on the dynamics of concentrated systems obtained by Crabb and Kovac² and by Crabb, Hoffman, Dial and Kovac³, however, suggest that this factor is of minor importance. The mean segment density in the theta region small enough that it is in the region where very little effect on the exponents was seen by Crabb and co-workers. Furthermore, in the multi-chain systems all three modes showed a similar change with increasing concentration, not the divergence of behavior observed by Downey and Kovac.

A second possibility is that the local stiffness of the lattice models results in short range expansion of the chains. If this is true, the dynamic scaling hypothesis would predict that the exponents characterizing the more local motions should be larger than their ideal chain values. This possibility can easily be tested by studying the dimensions of the chain in more detail. One of the purposes of this paper is to report the results of such a study. We have computed the mean square internal dimensions of the chain corresponding to the characteristic length scales of the first four normal modes and studied their dependence on chain length. Using the dynamic scaling hypothesis we can predict the effects of any local chain expansion on the relaxation times.

The third and most interesting possible explanation is that

the attractive energy results in long-lived pair contacts. The dynamic effects of long lived pair contacts in a semidilute solution were given the name "gel modes" by Brochard and DeGennes.⁴ In a semidilute system the long lived pair contacts cause the system to behave like a rubber, giving rise to a set of fast elastic modes. In the single chain system a different effect should be seen. Long lived pair contacts should slow down the natural relaxation behavior of the chain once the lifetime of the pair contact becomes comparable to the relaxation time of the motion. Since longer chains will have more pair contacts, this effect should become more important as the size of the molecules increases. This possibility can easily be tested in a computer simulation since the position of every chain segment is known at all times. The pair contacts can be identified and their lifetimes monitored. The second purpose of this paper is to report the results of a study of the distribution of lifetimes of pair contacts as a function of chain length and attractive energy.

We find that both local chain expansion and the lifetime of pair contacts contribute to the slowing of the $k = 3$ mode in the theta region and below. The face-centered cubic (FCC) lattice chains studied here do show short range expansion below the theta point, but not enough to explain the observed dynamic exponents. Both the average number of pair contacts and their average lifetime increase as the chain length and the strength of the attractive energy increase. The distribution of lifetimes of the pair contacts becomes significantly broader as the chain length

and attraction increase such that the tail of the distribution approaches times comparable to the relaxation time of the third mode. These results strongly suggest that the attractive interaction is altering the chain dynamics in the theta region. The simulation results reported here provide a possible explanation of recent experimental results on local segment dynamics in polyisoprene obtained by Waldow, et. al..⁵

MODEL

The simulation model used here was the FCC lattice model used by Downey and Kovac which is an extension of the original work of Downey, Crabb and Kovac⁶ and Naghizadeh and Kovac.⁷ The reader is referred to the original papers for a detailed description of the simulation algorithm. We studied chains of lengths 25, 49 and 73 beads at potentials, $\phi = -\epsilon/kT$, of 0.0, 0.10, 0.16 and 0.25. The theta point for FCC chains of this length is quite near a potential of 0.16, so we have data in the good solvent, theta and collapse regions as well as at one potential between full excluded volume and the theta point.

The local dimensions of the chain were determined by calculating the mean square distances, $\langle R^2_{1/k} \rangle$, of $1/2$, $1/3$ and $1/4$ the total number of bonds in the chain according to the formula

$$\langle R^2_{1/k} \rangle = T^{-1} \sum_{t=0}^T \frac{k}{N} \sum_i R^2_{i \lfloor \frac{N}{k} + i \rfloor} (t) \quad (2)$$

where t is the time in bead cycles, T is the total length of the simulation run, k is the mode number and N is the chain length. The chain length dependences of these dimensions were estimated by calculating the slope of a plot of $\ln \langle R^2_{1/k} \rangle$ vs. $\ln ((N-1)/k)$ to give a scaling exponent $2\nu_k$ defined as

$$\langle R^2_{1/k} \rangle \sim ((N-1)/k)^{2\nu_k} \quad (3)$$

To study the lifetime of the pair contacts we added a section to the program which identifies all nearest neighbor contacts (excluding beads adjacent along the chain contour) and

counts the number of bead cycles for which they remain unbroken. These data are collected in bins of various sizes to generate a histogram approximation to the distribution of lifetimes. The average lifetime of a pair contact $\langle t \rangle$ is calculated from the distribution according to the formula

$$\langle t \rangle = \left[\sum_t t n(t) \right] / \left[\sum_t n(t) \right] \quad (4)$$

where $n(t)$ is the number of contacts which survive for t bead cycles. The average number of pair contacts per bead cycle is calculated by dividing the total number of contacts by the total number of bead cycles in the run. All runs were 120,000N bead cycles in length. The data on the pair contact lifetimes were reproducible to within 1% from run to run. The normal coordinate relaxation times were also computed for each run to make sure that our results were consistent with the earlier results of Downey and Kovac. The agreement was good.

RESULTS AND DISCUSSION

The results for the internal mean square distances, $\langle R^2_{1/k} \rangle$ are listed in Table 1. The scaling exponents $2\nu_k$ for each k are listed in Table 2 along with the exponents α_k for the FCC lattice chains taken from the papers of Downey and Kovac. If the dynamic scaling hypothesis holds for the internal chain motions then α_k should be related to $2\nu_k$ as

$$\alpha_k = 2\nu_k + 1 \quad (5)$$

While equation (5) is reasonably well obeyed for the first three modes above the theta point and in the theta region it clearly breaks down in the collapse region for $k = 3$. The exponents show that there is a small amount of local chain expansion below the theta point, particularly for $k = 4$, but certainly not enough to explain the large dynamic exponents for $k = 3$ observed by Downey and Kovac.

Table 3 contains the distribution of pair contact times for the three chain lengths and four interaction energies studied. The results are reported as fraction of contacts which persist for a particular time span. The times are reported in units of N bead cycles. Table 4 lists the average lifetime of a pair contact, $\langle t \rangle$, and the average steady state number of pair contacts in the chain, $\langle n \rangle$.

Clearly both the average lifetime of a pair contact and the average number of contacts increases as the chain length and the strength of the attractive interaction increase. We performed a finite scaling analysis of the average lifetimes by plotting $\ln \langle t \rangle$ vs. $\ln (N-1)$ at constant ϕ . The plots are shown in Figure 1.

While it is dangerous to extract a power law relationship from such a small amount of data, we did compute the slopes of the double logarithmic plots and the exponents, $\delta(\phi)$, corresponding to a power law relationship of the form

$$\langle t \rangle \sim (N-1)^{\delta(\phi)} \quad (6)$$

are listed in Table 5. There is a significant increase in the exponent δ as the interaction energy increases. This parallels the trend seen in the exponent α_3 .

In a random system one would expect the average number of pair contacts to be proportional to the Boltzmann factor of the interaction energy, $\exp \phi$. The plot of $\ln \langle n \rangle$ vs. ϕ at constant N shown in Figure 2 shows that this is approximately true in this system. Figure 3 shows the chain length dependence of $\langle n \rangle$ at constant ϕ . The chain length dependence of $\langle n \rangle$ can be predicted by a simple dimensional argument. $\langle n \rangle$ should be proportional to the the probability of a contact times the volume of the polymer coil. In a mean field approximation this probability is proportional to the square of the segment density. The segment density is proportional to $N/\langle R^2 \rangle^{3/2}$. For an ideal chain one would expect that $\langle n \rangle$ would be proportional to $N^{1/2}$. In a good solvent $\langle n \rangle$ should be proportional to $N^{0.2}$, while in a poor solvent $\langle n \rangle$ should be proportional to N . Because the number of chain lengths studied was so small we did not attempt to verify these scaling relationships quantitatively. The plot does show clearly that the chain length dependence of $\langle n \rangle$ does become larger as ϕ increases, which is in qualitative agreement with the mean field argument. The dependence of $\langle t \rangle$ and $\langle n \rangle$ as a function

of chain length and potential does suggest that the exponent α_k might be effected by the finite lifetime of the pair contacts.

This possibility can be examined in more detail by looking at the distribution of the pair contact lifetimes as a function of attractive interaction and chain length. Figures 4-6 are semilog plots of the distribution of pair contact lifetimes. As the attractive interaction is increased the distribution broadens significantly and extends to longer and longer times. In the theta region and below there are a few pair contacts which remain unbroken for times of the order of the relaxation time for the $k = 3$ normal mode. These long-lived contacts seem to have a significant influence on the relaxation of the $k = 3$ mode, slowing it relative to the prediction of the dynamic scaling hypothesis.

The physical picture we have is that the attractive potential causes some of the pair contacts to persist long enough to slow the natural motion of the $k = 3$ mode. This mode must occasionally "wait" for a pair contact to break before it can relax toward equilibrium. The longer wavelength motions are not affected because they are much slower. The frequency of the making and breaking of pair contacts is much faster than the frequency of the long wavelength modes and therefore has no significant effect on their motions. Longer chains have more pair contacts with a longer average lifetime. This will cause the motions of the longer chains to be slowed even more than the shorter. This is consistent with an increased dynamic scaling exponent for the $k = 3$ mode. We have not yet been able to

convert this physical picture into a quantitative theory but we find it quite compelling and consistent with the simulation results.

A possible objection to this explanation is that there are very few contacts that live for the very longest times, certainly not enough to ensure that there will be one present at all times. On the other hand, all that is required for our qualitative picture to be correct, is that the natural relaxation be impeded by the existence of the pair contacts and that the effect increases with both chain length and attractive energy. In this view, the entire long time portion of the distribution would be involved in altering the spectrum of relaxation times. Even with the quite detailed picture of the chain dynamics that we have developed here it is still not possible to discover the precise effects of the lifetime of the pair contacts. Further simulation work is clearly indicated, but more important is the construction of a tractable mathematical model which can assess the effect of the long lived contacts on the chain relaxation.

Since dynamic Monte Carlo lattice models are quite idealized it is reasonable to ask whether these effects can be observed in real systems. Some recent work by Waldow, et. al. provides possible experimental confirmation. In these experiments the motion of an anthracene probe located in the center of a polyisoprene chain was studied using an optical technique. The anthracene probes the motion of 20 or so monomer units in the center of the chain. Waldow et. al. found that the relaxation time of the probe was considerably slower in a theta solvent than

in a good solvent. They also found that there was strong molecular weight dependence in the theta solvent, but essentially no dependence on molecular weight in the good solvent. Last, they found that the apparent activation energy of the relaxation time has depended on the molecular weight in a theta solvent but was independent of molecular weight in a good solvent. In their paper Waldow, et al. used some simple equilibrium Monte Carlo calculations to suggest that the slowing of the motion was due to an increased segment density in the theta region. Our results suggest that the slowing might instead be due to the existence of long lived pair contacts in the theta region. The dynamics of the anthracene probe are strikingly similar to the behavior of the $k = 3$ mode observed by Downey and Kovac which we attribute mainly to the effects of long-lived pair contacts. We see a larger molecular weight dependence of the relaxation time in the theta region than in the good solvent region. We also see a stronger chain length dependence of $\langle n \rangle$ as the theta region is approached. This would explain the molecular weight dependence of the activation energy observed by Waldow et. al. since the activation energy should be proportional to the average number of contacts.

If this analysis is correct, we would expect to see effects of solvent quality on the dynamics of intermediate scale chain motions such as those studied by Waldow, et. al.. Unfortunately, the precise length and time scales at which the effects of long-lived pair contacts will be seen cannot be determined from our simulations. The hydrodynamic interaction, which is not included

in our model, could also have dramatic effects. The arguments made here are highly suggestive, but not conclusive. Further theoretical and experimental work on this topic is clearly needed.

CONCLUSION

A detailed examination of the conformation and dynamics of FCC lattice chains as a function of attractive interaction indicates that the lifetime of nearest neighbor pair contacts has a significant effect on the chain dynamics near the theta point. Both the average lifetime and the average number of pair contacts increases as the chain length and the strength of the attractive interaction increase. The distribution of lifetimes becomes significantly broader as the strength of the attractive interaction increases. These results provide a qualitative explanation for the significant slowing of the $k = 3$ normal mode in the theta region observed by Downey and Kovac. There is some internal chain expansion in this lattice model which accounts for some, but far from all, of the increase in relaxation times. These simulations have also provided an alternate explanation of the solvent effects on the dynamics of labelled polyisoprene chains observed by Waldow, et. al..

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TABLE 1: Values of the mean square internal distances $\langle R^2_{1/k} \rangle$ as a function of the pair interaction potential, ϕ .

		INTERACTION POTENTIAL ϕ			
		0.00	0.10	0.16	0.25
N=25	$\langle R^2 \rangle$	41.5	34.2	29.5	21.4
	$\langle R_{1/2}^2 \rangle$	19.8	16.8	14.8	11.5
	$\langle R_{1/3}^2 \rangle$	12.3	10.8	9.78	8.17
	$\langle R_{1/4}^2 \rangle$	8.74	7.82	7.25	6.35
N=49	$\langle R^2 \rangle$	95.8	74.2	55.0	32.3
	$\langle R_{1/2}^2 \rangle$	46.1	36.7	28.2	18.3
	$\langle R_{1/3}^2 \rangle$	28.8	23.7	19.4	14.0
	$\langle R_{1/4}^2 \rangle$	20.5	17.2	14.7	11.4
N=73	$\langle R^2 \rangle$	160.	117.	86.4	34.6
	$\langle R_{1/2}^2 \rangle$	76.8	58.4	43.8	20.6
	$\langle R_{1/3}^2 \rangle$	47.6	37.5	29.4	16.9
	$\langle R_{1/4}^2 \rangle$	33.7	27.3	22.2	14.6

TABLE 2: Values of the static scaling exponents, $2\nu_1$, and the dynamic scaling exponents, α_1 , taken from reference 1.

	INTERACTION POTENTIAL ϕ			
Value	0.00	0.10	0.16	0.25
$2\nu_1$	1.26	1.13	0.98	0.55
α_1	2.18	2.19	2.11	1.68
$2\nu_2$	1.23	1.14	0.99	0.61
α_2	2.26	2.12	2.07	2.01
$2\nu_3$	1.23	1.14	1.01	0.70
α_3	2.35	2.22	2.11	2.12
$2\nu_4$	1.23	1.14	1.03	0.77

TABLE 3: Distribution of pair contact times as a function of chain length, N , and interaction potential, ϕ .

(a) Chain length = 25

Time (N Bead Cycles)	INTERACTION POTENTIAL ϕ			
	0.00	0.10	0.16	0.25
	% Contacts	% Contacts	% Contacts	% Contacts
13.04-10.20	17.7	16.7	14.9	14.6
0.24-0.40	13.7	13.2	12.6	11.6
0.44-0.80	19.9	19.1	18.7	17.5
0.84-1.20	13.3	13.1	12.9	12.3
1.24-1.60	9.18	9.22	9.19	9.05
1.64-2.00	6.52	6.68	6.74	6.83
2.04-2.40	4.74	4.91	5.08	5.25
2.44-2.80	3.50	3.71	3.85	4.08
2.84-3.20	2.61	2.84	2.97	3.20
3.24-3.60	1.96	2.18	2.32	2.58
3.64-4.00	1.50	1.68	1.85	2.12
4.04-8.00	4.78	5.81	6.69	8.54
8.04-16.00	0.53	0.849	1.17	2.07
16.04-20.00	0.0095	0.0198	0.040	0.122
20.04-30.00	0.0018	0.0055	0.0141	0.0582

30.04-40.00	0.0004	0.0002	0.0010	0.0067
> 40.00	0.0000	0.0001	0.0002	0.0011

(b) Chain length = 49

Time (N Bead Cycles)	INTERACTION POTENTIAL ϕ			
	0.00	0.10	0.16	0.25
	% Contacts	% Contacts	% Contacts	% Contacts
0.02-0.51	37.0	34.8	33.0	29.1
0.53-1.02	21.2	20.5	19.8	18.1
1.04-1.53	13.2	13.1	12.9	12.3
1.55-2.04	8.57	8.75	8.83	8.73
2.06-4.08	14.5	15.7	16.6	18.0
4.10-6.12	3.80	4.60	5.33	6.93
6.14-8.16	1.15	1.56	2.01	3.15
8.18-10.20	0.374	0.576	0.840	1.56
10.22-15.31	0.187	0.349	0.604	1.48
15.33-20.41	0.0174	0.0470	0.101	0.390
20.84-40.82	0.0033	0.0109	0.0327	0.211
40.84-61.22	0.0000	0.0006	0.0006	0.0103
61.24-81.63	0.0000	0.0001	0.0000	0.0021
81.65-102.04	0.0000	0.0000	0.0000	0.0004
102.06-122.45	0.0000	0.0000	0.0000	0.0002
122.47-142.86	0.0000	0.0000	0.0000	0.0001
142.88-163.27	0.0000	0.0000	0.0000	0.0000

163.29-183.67	0.0000	0.0000	0.0000	0.0000
> 183.67	0.0000	0.0000	0.0000	0.0000

(c) Chain length = 73

Time (N Bead Cycles)	INTERACTION POTENTIAL ϕ			
	0.00	0.10	0.16	0.25
	% Contacts	% Contacts	% Contacts	% Contacts
0.0-0.34	26.9	25.2	23.6	20.4
0.36-0.68	18.2	17.4	16.4	14.5
0.70-1.03	12.9	12.5	12.0	10.9
1.04-1.37	9.40	9.30	9.08	8.49
1.38-2.74	19.7	20.2	20.5	20.4
2.75-4.11	7.31	8.08	8.84	9.98
4.12-5.48	3.03	3.65	4.29	5.48
5.49-6.85	1.33	1.76	2.24	3.25
6.86-10.27	1.00	1.48	2.14	3.80
10.29-13.70	0.169	0.314	0.574	1.42
13.71-27.40	0.0421	0.112	0.286	1.12
27.41-41.10	0.0004	0.0018	0.0112	0.0988
41.11-54.79	0.0000	0.0004	0.0014	0.0174
54.81-68.49	0.0000	0.0002	0.0003	0.0043
68.51-82.19	0.0000	0.0000	0.0001	0.0016
82.21-95.89	0.0000	0.0000	0.0000	0.0006
94.90-109.59	0.0000	0.0000	0.0000	0.0003

109.60-123.29	0.0000	0.0000	0.0000	0.0001
123.30-136.99	0.0000	0.0000	0.0000	0.0001
137.00-205.48	0.0000	0.0000	0.0000	0.0001
> 204.5	0.0000	0.0000	0.0000	0.0000

Table 4: Average lifetime of a pair contact, $\langle t \rangle$, and average steady state number of pair contacts, $\langle n \rangle$, as a function of chain length, N , and interaction potential, ϕ .

N	INTERACTION POTENTIAL ϕ							
	0.00		0.10		0.16		0.25	
	$\langle n \rangle$	$\langle t \rangle$	$\langle n \rangle$	$\langle t \rangle$	$\langle n \rangle$	$\langle t \rangle$	$\langle n \rangle$	$\langle t \rangle$
25	1.89	0.855	2.22	0.971	2.41	1.077	2.61	1.321
49	1.94	0.885	2.32	1.022	2.67	1.174	2.97	1.605
73	2.04	0.896	2.47	1.042	2.86	1.236	3.14	1.785

TABLE 5: Values of the scaling exponent, $\delta(\phi)$, defined in equation (6).

ϕ	$\delta(\phi)$
0.00	0.042
0.10	0.066
0.16	0.129
0.25	0.281

FIGURE CAPTIONS

Figure 1: Double logarithmic plot of the average lifetime of a pair contact, $\langle t \rangle$, as a function of the chain length, $(N-1)$ for four values of the interaction potential: $\phi = 0.0$ ($\circ$), $\phi = 0.10$ ($\otimes$), $\phi = 0.16$ ($\triangle$) and $\phi = 0.25$ ($\blacktriangle$).

Figure 2: Semi-logarithmic plot of the average number of pair contacts, $\langle n \rangle$, as a function of the interaction potential, ϕ , for the chain lengths: $N = 25$ ($\circ$), $N = 49$ ($\otimes$) and $N = 73$ ($\triangle$).

Figure 3: Plot of the average number of pair contacts $\langle n \rangle$ as a function of chain length $(N-1)$ at four values of the interaction potential: $\phi = 0.0$ ($\circ$), $\phi = 0.10$ ($\otimes$), $\phi = 0.16$ ($\triangle$) and $\phi = 0.25$ ($\blacktriangle$).

Figure 4: Semi-logarithmic plot of the distribution of pair contact lifetimes for a chain of length $N = 25$ for four values of the interaction potential: $\phi = 0.0$ ($\circ$), $\phi = 0.10$ ($\otimes$), $\phi = 0.16$ ($\triangle$) and $\phi = 0.25$ ($\blacktriangle$).

Figure 5: Semi-logarithmic plot of the distribution of pair contact lifetimes for a chain of length $N = 49$ for four values of the interaction potential: $\phi = 0.0$ ($\circ$), $\phi = 0.10$ ($\otimes$), $\phi = 0.16$ ($\triangle$) and $\phi = 0.25$ ($\blacktriangle$).

Figure 6: Semi-logarithmic plot of the distribution of pair contact lifetimes for a chain of length $N = 73$ for four values of the interaction potential: $\phi = 0.0$ ($\circ$), $\phi = 0.10$ ($\otimes$), $\phi = 0.16$ ($\triangle$) and $\phi = 0.25$ ($\blacktriangle$).

FIG. 1

Fig. 2

Fig 3

Fig 4

Fig. 5

Fig 6

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Equilibrium and Dynamic Properties of a Polymer Chain
in a Reflecting Wedge

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ABSTRACT

The equilibrium and dynamic properties of a single self-avoiding chain grafted to the intersection of two perpendicular reflecting walls were studied using a Monte Carlo method. The results for the equilibrium dimensions of the chain agree well with recent renormalization group calculations. For long chains the dynamic properties are predicted by the dynamic scaling hypothesis, although deviations are observed for short chains.

INTRODUCTION

In a recent paper Hahn and Kovac¹ studied the equilibrium and dynamic properties of a single polymer chain terminally attached to an infinite reflecting boundary using a Monte Carlo method. The equilibrium properties of the chain were in reasonable agreement with renormalization group (RG) calculations². The end-to-end vector relaxation times for the tethered chain adhered to the dynamic scaling hypothesis for all chain lengths studied, although the reflecting boundary did induce a chain length independent slowing of the chain motion.

Recent renormalization group calculations of the equilibrium properties of chains interacting with more than one surface³ have stimulated us to study the equilibrium and dynamics properties of a single chain terminally attached to the junction of two perpendicular reflecting surfaces, a chain in a wedge. There were two reasons for undertaking this study. First, we wanted to provide simulation data of the equilibrium dimensions of the chain in order to compare with the RG calculations. Second, we were interested in seeing whether the dynamic scaling relation would hold in this more confined situation. The general question of the effects of interfaces on the motions of polymer chains has been little studied. The motion of the chain in a wedge is the logical extension of our earlier paper on the effects of a single surface on the chain dynamics.

We find that the equilibrium properties of the chain are in reasonable agreement with the RG calculations just as in the single wall case. The dynamics, however, are somewhat different. We find that short chains do not follow the dynamic scaling hypothesis exactly. The second confining wall slows the chain motions. As the chain

becomes longer the effect of the wall decreases and for sufficiently long chains the dynamic scaling relation does again provide a link between the equilibrium and dynamic properties of the chain.

MODEL

The model chosen for this study was the face-centered cubic (FCC) lattice model developed by Downey, Crabb and Kovac.⁴ An FCC chain was permanently attached to the intersection of two perpendicular impenetrable (reflecting) walls. The dynamics of the chain were simulated using the Downey-Crabb-Kovac model with the additional restriction that no bead was allowed to intersect either surface. Simulations of the equilibrium properties were done for chains of lengths 35 - 215 bonds with excluded volume. Because of the very long simulation runs needed to study the end-to-end vector relaxation, dynamic properties were only studied for chains of lengths 35 - 107 bonds. (One chain length without excluded volume was run in order to verify that the simulation algorithm corresponded to reflecting boundary conditions.) No hydrodynamic interactions were included. The mean square end-to-end distance $\langle R^2 \rangle$ and the end-to-end vector autocorrelation function, $C(t) = \langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle$, were calculated for each simulation run. As usual, the ensemble averages were approximated as time averages over a simulation run begun from a fully equilibrated conformation. The end-to-end vector relaxation time was estimated by fitting an unweighted least squares line to the linear long time portion of a semilog plot of $C(t)$ vs. t . Generally, at least ten runs were done for each chain length in order to estimate the error.

RESULTS AND DISCUSSION

The results for the mean square end-to-end distances of the terminally attached chains with excluded volume, $\langle R^2 \rangle_g$, are collected in Table 1 along with the results for free chains $\langle R^2 \rangle_f$ of the same length. In the final column the ratio $\gamma_{R^2} = \langle R^2 \rangle_g / \langle R^2 \rangle_f$ has been computed. The average of this for all chain lengths is $1.74 \pm .04$. There appears to be no systematic variation with chain length. We calculated this ratio for a chain of length $N = 72$ without excluded volume and found a value of $\gamma_{R^2} = 1.0$. This verifies that our simulation indeed represents the case of reflecting walls. While not an exact comparison, recent renormalization group calculations for a chain in a 90° wedge formed by two repulsive walls give a ratio of 1.61^5 , which is quite close to our value.

We also calculated the scaling exponent 2ν by making double logarithmic plots of $\langle R^2 \rangle$ vs. $(N-1)$ and determining the slope of an unweighted least squares line. This slope corresponds to the exponent in the scaling relation

$$\langle R^2 \rangle \sim (N-1)^{2\nu} \quad (1)$$

The values of the exponent 2ν is 1.19 for the grafted chains and 1.17 for the free chains. These values are in excellent agreement with the expected value of 1.2.

The values of the end-to-end vector relaxation times, τ_R , are listed in Table 2. For a chain grafted to a single plane reflecting surface Hahn and Kovac found that the relaxation time obeyed the dynamic scaling relation

$$\tau_R \sim \langle R^2 \rangle (N-1) \quad (2)$$

To test this hypothesis for the two wall case we computed the ratio $S_N = \tau_R / \langle R^2 \rangle (N-$

1). These values are also listed in Table 2 and plotted as a function of N^{-1} in Figure 1. Clearly the dynamic scaling ratio is not constant at short chain lengths, but appears to approach a constant value at the longest chain lengths studied. A quadratic extrapolation to infinite chain length provides a limiting value for the ratio of $S_{\infty} = 0.268$. It is clear that the confining walls do slow the relaxation time in addition to their effect on the chain conformation, but this effect disappears as the chains become very long. This differs from the single wall case where the ratio S_N was essentially independent of chain length even for the shortest chain lengths studied.

For the simple case of self avoiding chains confined by reflecting walls it appears that the major effect of the walls on the chain dynamics is predicted by the dynamic scaling hypothesis, although there are corrections for short chains confined by two walls. We are currently extending our algorithms to study both attractive walls and self attracting chains where quite different effects might well be observed.

REFERENCES

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Table 1: Values of the mean-square end-to-end distance $\langle R^2 \rangle$ for free and grafted chains as a function of chain length, $N-1$. In the final column is the ratio $\gamma_{R^2} = \langle R^2 \rangle_g / \langle R^2 \rangle_f$.

$N-1$	$\langle R^2 \rangle_f$	$\langle R^2 \rangle_g$	γ_{R^2}
35	65.9	116.	1.78
53	110.	186.	1.71
71	154.	263.	1.70
107	243.	426.	1.75
143	350.	594.	1.70
179	470.	818.	1.74
199	530.	922.	1.74
215	574.	1010	1.76

Table 2: Values of the end-to-end vector relaxation time τ_R and the dynamic scaling ratio S_N as a function of chain length, $N-1$.

$N-1$	τ_R	$S_N = \tau_R / \langle R^2 \rangle (N-1)$
35	1160	0.287
53	2740	0.277
71	5170	0.272
107	12500	0.270

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