Macromolecules **1991,** *24,* 3883-3887

Role of Attractive Forces in the Dynamics of Polymer Chains near the Θ Point

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Received October 8, 1990; Revised Manuscript Received February 26, 1991

ABSTRACT: The role of attractive forces in the dynamics of lattice model chains near the Θ point has been investigated by 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 nonadjacent 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 de Gennes. The simulation results also provide an alternative explanation of some recent experimental results concerning the relaxation of anthracene-labeled polyisoprene chains.

Introduction

In two recent publications Downey and Kovac studied the dynamics of lattice models of polymer chains in the Θ 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 Θ condition by the addition of an attractive nearest-neighbor interaction between adjacent nonbonded 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

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

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 Θ region, the exponent characterizing the shortest mode studied, α_3, decreased much more slowly as the Θ point was approached from above, never becoming as small as 2.0. In the collapse region below the Θ 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 Θ region and below then 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 Θ region is causing the exponent α_3 to increase. Previous results on the dynamics of concentrated systems obtained by Crabb and Kovac[2] and by Crabb, Hoffman, Dial, and Kovac,[3] however, suggest that this factor is of minor importance. The mean segment density in the Θ region is 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 multichain 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 de Gennes.[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 Θ region and below. The face-centered cubic (FCC) lattice chains studied here do show short-range expansion below the Θ 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

0024-9297/91/2224-3883$02.50/0

Table I
Values of the Mean-Square Internal Distances $\langle R_{1/k}^2\rangle$ 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 II
Values of the Static Scaling Exponents, $2\nu_l$, and the Dynamic Scaling Exponents, α_l, Taken from Reference 1

	interaction potential ϕ			
	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

attractive interaction is altering the chain dynamics in the Θ 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 Kovac[6] 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 Θ point for FCC chains of this length is quite near a potential of 0.16, so we have data in the good solvent, Θ, and collapse regions as well as at one potential between full excluded volume and the Θ point.

The local dimensions of the chain were determined by calculating the mean-square distances, $\langle R_{1/k}^2\rangle$, of $^1/_2$, $^1/_3$, and $^1/_4$ the total number of bonds in the chain according to the formula

$$\langle R_{1/k}^2\rangle = T^{-1}\sum_{t=0}^{T}\frac{k}{N}\sum_{i}R_{i[N/k+i]}^{\;2}(t) \tag{2}$$

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 $\ln\langle R_{1/k}^2\rangle$ vs $\ln[(N-1)/k]$ to give a scaling exponent $2\nu_k$ defined as

$$\langle R_{1/k}^2\rangle \sim [(N-1)/k]^{2\nu_k} \tag{3}$$

To study the lifetime of the pair contacts, we added a section to the program that 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

$$\langle t\rangle = [\sum_{t} t n(t)]/[\sum_{t} n(t)] \tag{4}$$

where $n(t)$ is the number of contacts that survive for t bead cycles. The average number of pair contacts per bead cycle is calculated by dividing the total number of

Table III
Distribution of Pair-Contact Times as a Function of Chain Length, N, and Interaction Potential, ϕ

	% contacts for interaction potential ϕ			
time (N bead cycles)	0.00	0.10	0.16	0.25
(a) Chain Length = 25				
0.04–0.20	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				
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				
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 IV
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

	interaction potential ϕ							
	0.00		0.10		0.16		0.25	
N	$\langle n \rangle$	$\langle t \rangle$	$\langle n \rangle$	$\langle t \rangle$	$\langle n \rangle$	$\langle t \rangle$	$\langle n \rangle$	$\langle t \rangle$
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

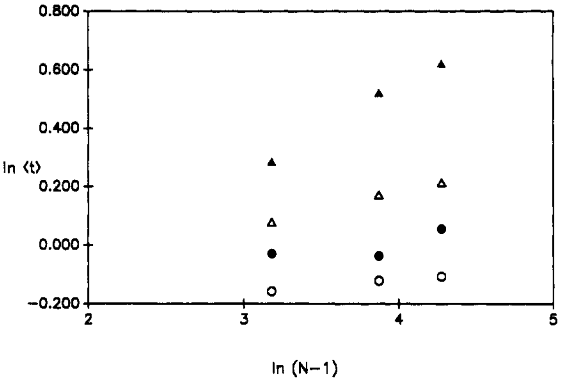

Figure 1. Double-logarithmic plot of the average lifetime of a pair contact, $\langle t \rangle$, as a function of the chain length $(N-1)$ for four values of the interaction potential: $\phi = 0.0$ (○), $\phi = 0.10$ (●), $\phi = 0.16$ (△), and $\phi = 0.25$ (▲).

Table V
Values of the Scaling Exponent, $\delta(\phi)$, Defined in Equation 6

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

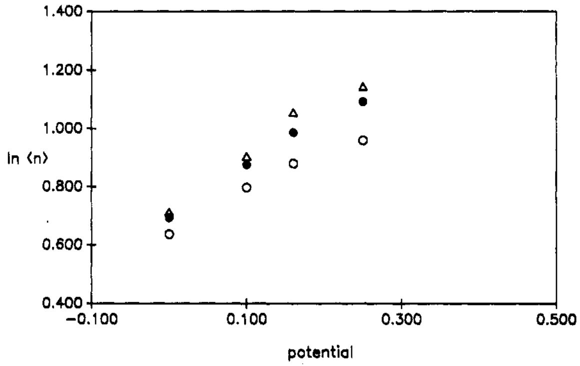

Figure 2. Semilogarithmic plot of the average number of pair contacts, $\langle n \rangle$, as a function of the interaction potential, ϕ, for the chain lengths: $N = 25$ (○), $N = 49$ (●), and $N = 73$ (△).

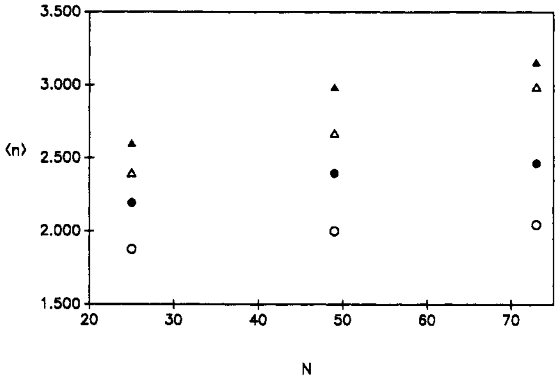

Figure 3. Plot of the average number of pair contacts, $\langle n \rangle$, as a function of chain length $(N-1)$ at four values of the interaction potential: $\phi = 0.0$ (○), $\phi = 0.10$ (●), $\phi = 0.16$ (△), and $\phi = 0.25$ (▲).

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, $\langle R_{1/k}{}^2 \rangle$ are listed in Table I. The scaling exponents $2\nu_k$ for each k are listed in Table II 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

$$\alpha_k = 2\nu_k + 1 \tag{5}$$

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

Table III contains the distribution of pair contact times for the three chain lengths and four interaction energies studied. The results are reported as the fraction of contacts that persists for a particular time span. The times are reported in units of N bead cycles. Table IV 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 naive 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

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

are listed in Table V. 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 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.

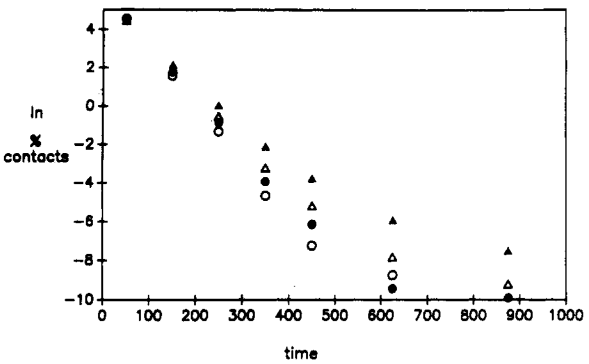

Figure 4. Semilogarithmic plot of the distribution of pair contact lifetimes for a chain of length $N = 25$ for four values of the interaction potential: $\phi = 0.0$ (○), $\phi = 0.10$ (●), $\phi = 0.16$ (△), and $\phi = 0.25$ (▲).

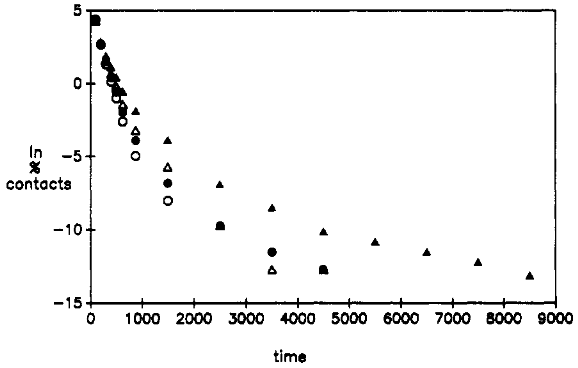

Figure 5. Semilogarithmic plot of the distribution of pair contact lifetimes for a chain of length $N = 49$ for four values of the interaction potential: $\phi = 0.0$ (○), $\phi = 0.10$ (●), $\phi = 0.16$ (△), and $\phi = 0.25$ (▲).

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 Θ region and below there are a few pair contacts that remain unbroken for times on 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.

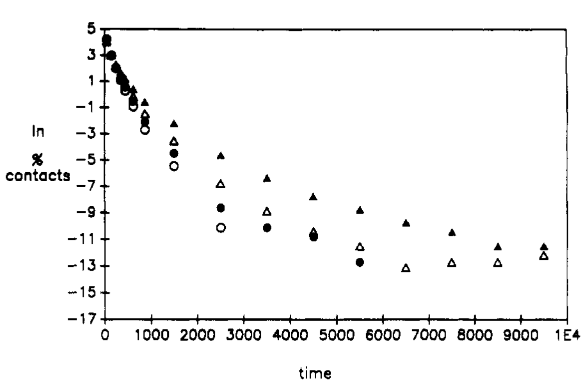

Figure 6. Semilogarithmic plot of the distribution of pair contact lifetimes for a chain of length $N = 73$ for four values of the interaction potential: $\phi = 0.0$ (○), $\phi = 0.10$ (●), $\phi = 0.16$ (△), and $\phi = 0.25$ (▲).

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 that 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 by 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 Θ solvent than in a good solvent. They also found that there was strong molecular weight dependence in the Θ 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 Θ 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 Θ region. Our results suggests that the slowing might instead be due to the existence of long-lived pair contacts in the Θ 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 Θ region than in the good solvent region. We also see a stronger chain-length dependence of $\langle n \rangle$ as the Θ 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 Θ point. Both the average lifetime and the average number of pair contacts increase 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 Θ 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 labeled polyisoprene chains observed by Waldow et al.

Acknowledgment is made to the U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Sciences, for financial support of this work. J.K. thanks Mark Ediger for useful discussions concerning the experiments on polyisoprene dynamics.

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