Notes

Dynamics of Lattice Models of Polymer Chains in the Collapse Region

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Introduction

In previous studies we have performed dynamic Monte Carlo simulations for self-avoiding isolated chains with fixed bond lengths and nearest-neighbor interactions between nonbonded beads of the chain. Simulations were performed using both simple cubic (SC)[2-4] and face-centered cubic (FCC)[4] lattice models. The purpose of these studies was to try to understand the dynamic cancellation of the effects of the excluded volume by the attractive pair potential. A wide range of potentials were studied, from good solvent conditions to the collapsed chain regime. At temperatures above the Θ point, the dynamic scaling results showed a predictable model dependence. It was found that for both the SC and FCC models the dynamic scaling exponents obtained were equal for a given value of $\mu\phi$, where μ is the coordinator number minus 1 and ϕ is the negative of the nearest-neighbor potential divided by k_BT. This is the same behavior that was seen by Mazur and McCrackin for the static properties of the chain.[5] As the Θ point was passed, the dynamic scaling exponents for simple cubic and face-centered cubic lattice models began to differ. The primary reason for this difference was thought to be the two-bead elementary motions required for reasonable dynamics in the SC model. At the higher segment concentrations near the Θ point the two-bead motions will be suppressed compared to the single-bead motions. It had been previously shown that athermal FCC and SC models with elementary motions identical with those used in the studies of the Θ region had identical dynamic scaling behavior for isolated chains.[6] At high concentrations, however, there were differences consistent with the elimination of successful two-bead motions in the SC model.[7,8]

The results in the Θ region and below were consistent with the formation of gel modes predicted by Brochard and de Gennes,[1] but several other factors such as local chain stiffness, internal chain expansion, and increased segment density in the collapsed coil could also explain the change in the chain dynamics as the intersegment potential is made more attractive.[4] In order to investigate this further we have conducted an investigation of the internal dynamics of collapsed chains. In collapsed chains the effect of the gel modes, if they exist, should be even more dramatic. The model dependence observed below the Θ point also requires further investigation.

Previous results on athermal chains[9,10] would indicate that the FCC and body-centered cubic (BCC) lattice models used in this work should exhibit the same scaling behavior since both models use similar one-bead elementary motions and both models show identical behavior in the good solvent regime. This must be checked, however, since there have been no previous studies of the lattice dependence of the internal dynamics of such tightly coiled chains. Comparison of the behavior of these two models with that of the simple cubic lattice model should also provide further insight into the role of the two-bead motions in the dynamics of tightly coiled chains.

The only other Monte Carlo study of the dynamics of a collapsed chain is an off-lattice simulation by Baumgartner.[11,12] This study used freely jointed chains of up to 64 beads interacting through a Lennard-Jones potential. Although his main interest was the static properties, Baumgartner did report that the density fluctuations below the Θ point were not consistent with the dynamic scaling hypothesis. At very low temperature he observed a glasslike transition and reptation dynamics.

In this paper we report the results of dynamic Monte Carlo simulations of the internal motions of both face-centered and body-centered cubic lattice models of polymer chains in the collapse region. We have determined the relaxation times of the first three Rouse normal coordinates and studied their dependence on temperature, chain length, and mode number. We find that the two models have the same dynamic behavior at a given value of $\mu\phi$ just as they do in the good solvent regime. We also find that the dependence of the relaxation times on temperature is consistent with the existence of gel modes as predicted by Brochard and de Gennes.[1]

Simulation Models

The FCC model used in this study was described in a previous paper to which the reader is referred for details.[4] The BCC model is a straightforward extension of the athermal BCC model developed by Downey and Kovac.[10] The details of the elementary motions can be found in that paper. The autocorrelation functions of the first three Rouse coordinates[13] were calculated as time averages over simulation runs of 30 000 samples. The relaxation times of the Rouse modes were determined as described in previous work. All relaxation times are averages of at least four runs.

Results and Discussion

The relaxation times of the first three normal coordinates are shown in Table I. They were fit to the scaling relaxation below by an unweighted least-squares fit of ln τ vs ln $(N-1)$. The slope of this line corresponds to the scaling exponent, α_k, defined by the relation

$$\tau(N,k) \sim (N-1)^{\alpha_k} \tag{1}$$

The values of α_k obtained for the two lattices for three values of $\mu\phi$ are listed in Table II and are also plotted in Figure 1. The dynamic scaling hypothesis predicts

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

where $\langle R^2 \rangle$ is the mean-square end-to-end distance of the chain. For a completely collapsed chain, $2\nu = {}^2/_3$. The value for α_1 obtained here is approximately ${}^5/_3$, in

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Table I
Relaxation Times of the First Three Normal Modes as a Function of Chain Length, N, and Scaled Interaction Potential, $\mu\varphi = -\mu\epsilon/k_BT$

lattice type	N	$\mu\phi$ = 2.75			$\mu\phi$ = 3.30			$\mu\phi$ = 3.85		
		τ_1	τ_2	τ_3	τ_1	τ_2	τ_3	τ_1	τ_2	τ_3
BCC	24	212	79.6	42.2	211	85.8	47.9	197	95.5	58.2
BCC	36	511	197	110	418	215	138	400	230	167
BCC	48	815	363	208	697	414	273	629	490	384
BCC	60	1230	546	353	956	812	633	1080	812	633
FCC	24	180	64.4	33.6	167	69.2	38.7	154	76.1	46.0
FCC	36	399	157	88.4	346	172	107	324	196	137
FCC	48	641	285	173	540	311	216	522	353	273
FCC	60	920	471	288	819	510	360	792	627	460

Table II
Scaling Exponents α_k as a Function of the Effective Potential, $\mu\varphi = -\mu\epsilon/k_BT$[a]

$\mu\phi$	α_1		α_2		α_3	
	BCC	FCC	BCC	FCC	BCC	FCC
2.75	1.85 (0.9981)	1.73 (0.9990)	2.06 (0.9994)	2.10 (0.9990)	2.25 (0.9999)	2.28 (1.0000)
3.30	1.62 (0.9994)	1.67 (0.9996)	2.17 (0.9999)	2.11 (0.9999)	2.41 (0.9997)	2.37 (0.9999)
3.85	1.77 (0.9965)	1.73 (0.9998)	2.29 (0.9991)	2.21 (0.9993)	2.57 (0.9993)	2.57 (0.9995)

[a] The correlation coefficient for the least-squares fit from which the α_k value was obtained is listed below that value in parentheses.

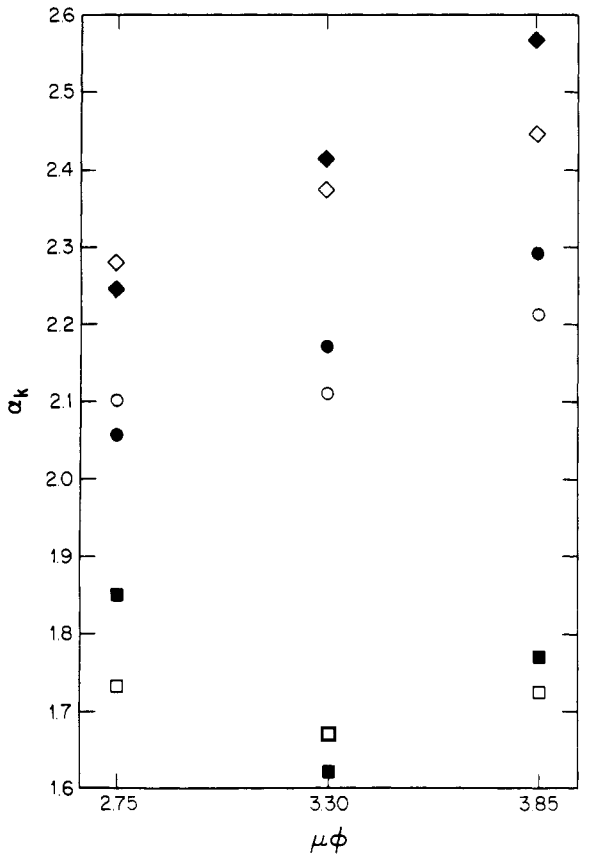

Figure 1. Values of α_k vs $\mu\phi$ for k = 1 (□), k = 2 (○), and k = 3 (◇). Open symbols are for the FCC model. Closed symbols are for the BCC model.

agreement with this hypothesis. The values of $\langle R^2\rangle$ obtained, however, did not obey a scaling law as a function of chain length in the collapse region. For tightly coiled chains the mean-square radius of gyration, $\langle S^2\rangle$, may be a better measure of the static properties, at least in terms of scaling behavior. This has previously been reported[11,14] and is a question that we plan to investigate further.

In this collapsed region it is apparent that there are large differences in α_1, α_2, and α_3, such that α_k increases with increasing k. Both models exhibit identical behavior for a given value of $\mu\phi$. This indicates that the relaxation of the short-range motions is becoming more inhibited relative to long-range motions as the chain length increases. Short-range stiffness of the chain would slow the relaxation, particularly for smaller chains and higher modes, but it is unlikely to account for a such a large dependence of α_k on k since in athermal systems we found only small differences in α_k for different k.[10] It is possible that the chains exhibit internal expansion such as that seen by Curro and Schaefer,[15] but such effects are not likely to be large enough to be responsible for the dramatic effects seen here. Neither is this behavior likely to be entirely due to density effects. A previous study on an FCC model showed α_k to have only a small k dependence at high concentrations.

The most likely cause of the large dependence of α_k on k is the great increase in the lifetime of nearest-neighbor pair contacts for the increasingly collapsed long chains. Brochard and de Gennes[1] have predicted that, as the mean lifetime of nearest-neighbor contacts approaches the relaxation time of a mode, the relaxation time of that mode should increase dramatically, resulting in the creation of so-called "gel modes". In Table III are listed the coil densities, ρ, determined from the measured mean-square end-to-end distance by the equation

$$\rho = 3N/4\pi\langle R^2\rangle^{3/2} \tag{3}$$

From Table III it is obvious that the longer chains are much more tightly coiled than the shorter ones and therefore should have long-lived nearest-neighbor contacts. If Brochard and de Gennes are correct, this would result in unusually large values for relaxation times of the higher modes in the long chains, which in turn implies an increase in α_k with increasing k. The large dependence of α_k on k observed here is strong evidence for the existence of these gel modes.

The relaxation times listed in Table I also show evidence of the existence of gel modes. As the potential increases, the relaxation times of the higher modes increase while the relaxation times of the first mode change very little. For the most attractive potentials and longest chains (i.e., highest coil densities) the relaxation times seem to be converging toward a single value.

The relaxation times were also fit to the scaling relation given in eq 4 by means of an unweighted least-squares fit of ln τ vs ln k. The values of γ_N obtained for

$$\tau(N,k) \sim k^{-\gamma_N} \tag{4}$$

the two models are listed in Table IV and plotted in Figure 2. From the data it is apparent that within the limits of the study the two models give the same scaling

Table III
Values Obtained for the Mean Coil Densities, ρ_N, as a Function of Chain Length, N, and Scaled Potential, $\mu\varphi = -\mu\epsilon/k_BT$

	ρ_N							
	$N = 24$		$N = 36$		$N = 48$		$N = 60$	
$\mu\phi$	BCC	FCC	BCC	FCC	BCC	FCC	BCC	FCC
2.75	0.0580	0.0613	0.0567	0.0615	0.0628	0.0682	0.0681	0.0773
3.30	0.0731	0.0811	0.0930	0.0980	0.1078	0.1180	0.1355	0.1370
3.85	0.0986	0.1118	0.1384	0.1447	0.1657	0.1839	0.1967	0.2087

Table IV
Scaling Exponents γ_N as a Function of the Effective Potential $\mu\varphi = -\mu\epsilon/k_BT$[a]

	γ_{24}		γ_{36}		γ_{48}		γ_{60}	
$\mu\phi$	BCC	FCC	BCC	FCC	BCC	FCC	BCC	FCC
2.75	1.462	1.520	1.398	1.369	1.236	1.190	1.138	1.048
	(−0.9996)	(−0.9998)	(−0.9999)	(−0.9999)	(−0.9990)	(−0.9999)	(−0.9998)	(−0.9981)
3.30	1.345	1.325	1.001	1.058	0.843	0.831	0.644	0.740
	(−0.9996)	(−0.9995)	(−0.9999)	(−0.9992)	(−0.9990)	(−0.9993)	(−0.9998)	(−0.9981)
3.85	1.102	1.093	0.797	0.778	0.440	0.589	0.482	0.478
	(−0.9991)	(−0.9986)	(−1.000)	(−0.9984)	(−0.9898)	(−0.9995)	(−0.9942)	(−0.9741)

[a] The correlation coefficient for the least-squares fit from which the γ_N value was obtained is listed below that value in parentheses.

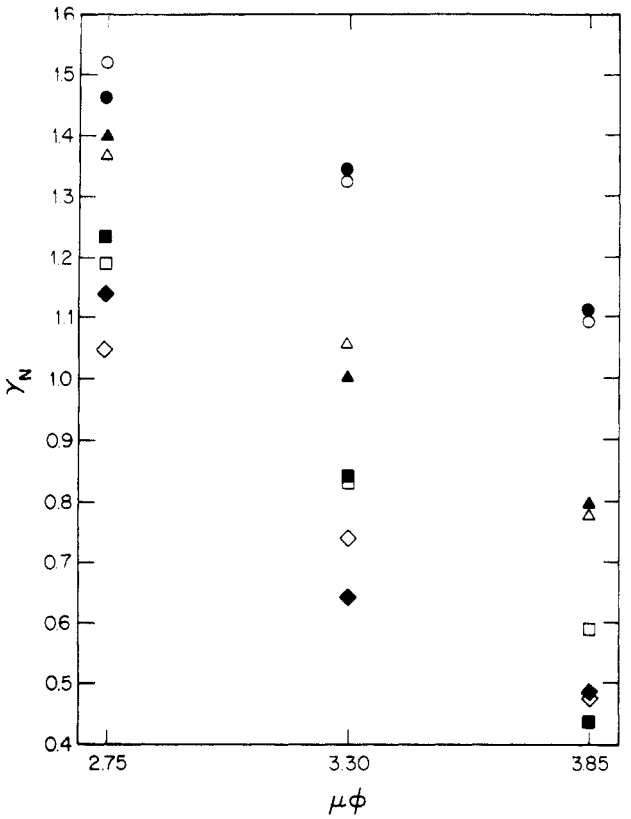

Figure 2. Values of γ_N vs $\mu\phi$ for $N = 24$ (○), $N = 36$ (△), $N = 48$ (□), and $N = 60$ (◇). Open symbols are for the FCC model. Closed symbols are for the BCC model.

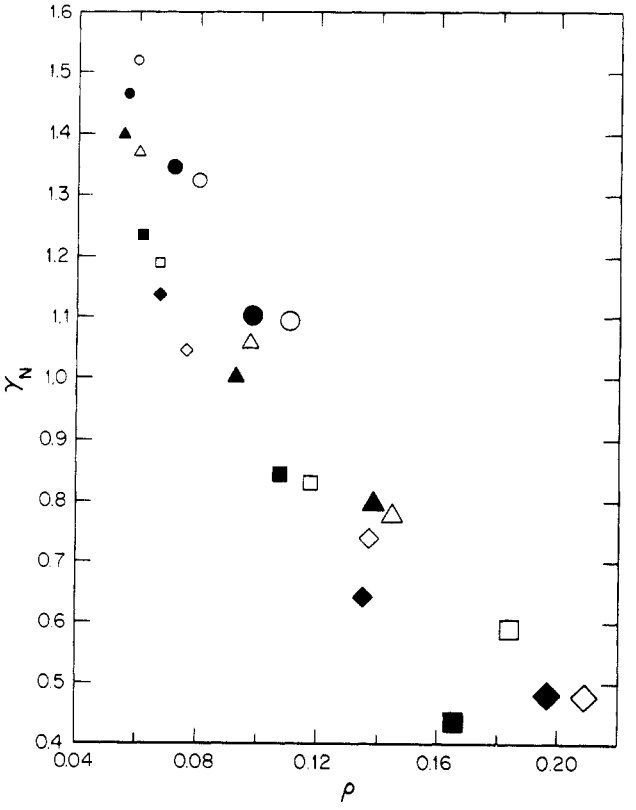

Figure 3. Values of γ_N vs ρ for $N = 24$ (○), $N = 36$ (△), $N = 48$ (□), and $N = 60$ (◇). Open symbols are for the FCC model. Closed symbols are for the BCC model. Increasingly large symbols indicate increasingly attractive pair interaction.

exponent for a given value of $\mu\phi$. We find that as the attraction increases the dependence of γ_N on N also increases; for larger N, γ_N is smaller. These data indicate that the higher coil densities result in greater inhibition of shorter range motions relative to the longer range motions, which is consistent with the existence of gel modes.

A comparison of the γ_N values in Table IV with the coil densities, ρ, in Table III shows a strong correlation between γ_N and ρ. This is even more evident in the plot of γ_N vs ρ in Figure 3. From the graph it can be seen that there is a nearly linear relationship between γ_N and ρ, which is only weakly dependent on chain length or potential. Most of the data points lie relatively close to the same straight line. This correlation between the static property, the segment density, and the dynamic property, the exponent γ_N, has not been reported before, to the best of our knowledge.

Conclusions

The dynamic scaling exponents showed the same dependence on lattice coordination number as seen by Mazur and McCrackin[5,14] for static properties of the chain. This provides good evidence that the previously observed differences in the FCC and SC models in the collapsed regime are due to the preferential suppression of two-bead elementary motions used in the SC model as the interaction potential is made more attractive. The effect of the attractive potential on the two-bead motions is similar

to the density effects seen by Crabb et al.[7] The FCC and BCC models both have only one-bead elementary motions and therefore show the same scaling behavior as a function of the attractive potential.

The behavior of the chain dynamics in the Θ and collapse regions seem to be nicely explained by the formation of gel modes predicted by Brochard and de Gennes. At very large attractive values of the potential and corresponding high coil densities the differences in the values of the relaxation times of the three modes are becoming significantly smaller. The scaling exponent, γ_N, showed a nearly linear correlation with the coil density, ρ, independent of chain length and the value of the potential. This has not been previously observed. In future work, the lifetime of pair contacts will be measured to further investigate the existence of gel modes.

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Effect of Ionic Aggregation on Ionomer Chain Dimensions. 2. Sulfonated Polyurethanes

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I. Introduction

The effect of ionic aggregation on ionomer chain dimensions is an area into which much theoretical effort has flowed, but experimental work has been quite limited. In a parallel small-angle neutron scattering (SANS) study of carboxy-telechelic polystyrene ionomers, we found no change in the average chain dimension as a result of ionic aggregation.[1] This finding agrees with the theory of Squires et al.[2] but disagrees with the theories of Forsman[3] and Dreyfus,[4] both of which predict substantial chain expansion. Here, we examine a sulfonated polyurethane ionomer with labeled soft segments [poly(tetramethylene oxide) (PTMO)]. The polyurethane ionomer differs in three important ways from the telechelics. First, instead of bearing only one ionic group at each chain end, the polyurethane ionomer contains many pendant groups spaced along the chain, separated by the soft-segment units. Second, the ionic groups here are sulfonates rather than carboxylates; the former are known to be more strongly interacting.[5] Third, and perhaps most important, the ion content of the polyurethane ionomers is much greater than that of the telechelics: their equivalent weight is about 775 g/equiv vs 3500 g/equiv for the telechelics. Since the relative chain expansion is predicted to increase with ion content, some chain expansion may be discernible here, though it was not with the telechelics.

As a reference for the unperturbed dimensions of the soft segment, blends of the PTMO oligomers were used. Since these materials have low degrees of polymerization N and do not have a particularly narrow molecular weight distribution (MWD), a polydisperse wormlike chain model described earlier[1] was used to fit the data. The polydispersity introduces the possibility that the chains may not have their unperturbed conformations, even in bulk, due to swelling of the longer chains by the shorter ones, as has been noted previously for poly(dimethylsiloxane) in a solution of its oligomer.[6]

II. Experimental Section

The deuterous PTMO was synthesized as described previously[7] from fully deuterous monomer (99.5+ atom % D, Aldrich). The hydrogenous PTMO was a commercial sample (N_n = 14.03 by end-group titration). The MWD of the deuterous oligomer was determined by a high-performance liquid chromatographic (HPLC) method[7] and is shown in Figure 1 up to N = 51. For calculating moments of N and for the polydisperse wormlike chain model describing the coherent SANS, the MWD was extrapolated through N = 150 by fitting the data over the range N = 12–51 to a straight line in log(mole fraction) vs N. Moments of N and R_g^2, calculated with a (the Kuhn, or statistical segment, length) equal to both 18.8 and 24.1 Å, are listed in Table I. The choice of a values comes from the SANS results as described below. Blends of the two oligomers, with deuterous volume fractions v_D near 0.2 and 0.5, were prepared by blending the two oligomers in methanol (10 wt %) and stirring for 7 h. The methanol was then evaporated in an air oven at 80 °C for 5 h and finally in a vacuum oven at 40 °C for 9 h. The melting point of the oligomers is very close to room temperature, so to prevent any crystallization (which could also lead to

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