

SHORT COMMUNICATIONS

**Monte Carlo Simulation of Dynamics of Concentrated Polymer System<sup>†</sup>**

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Lattice models have been extensively used to estimate equilibrium dimensions of polymer chains. These models may also be used to simulate dynamical properties of polymer chains. The dynamics of polymers are discussed in terms of two models which are supposed to describe the motions of chains at the two extremes of behavior. In dilute solution the relaxation of chains may be studied using a lattice model of the chain and simple local chain-movement rules to simulate the random collisions of the chain with solvent molecules.<sup>1-5</sup> In bulk solution the reptation model of De-Gennes is ordinarily used.<sup>6-7</sup> Despite the reptation model has been very fruitful and has received considerable experimental support,<sup>8</sup> the reptation hypothesis remains controversial, especially at high concentration. Many investigators have studied the dynamics of chains in entangle systems.<sup>9-13</sup> These investigations indicate that a description of the chain internal motions in terms of the Rouse coordinate is adequate even in the range of concentrations.<sup>12</sup> Much of the discussion centers around the chain length dependence of the relaxation time. They present the scaling exponents  $\alpha$ , which characterize their variation with chain length for a given

concentration, expressed by the scaling law  $T \sim (N-1)^\alpha$ , and the exponents  $\alpha$  increase with concentration. We notice that the dynamics of chains in entangle systems depends strongly on the concentration. Here we aim to investigate the concentration dependence of the relaxation quantitatively. In the present paper, we report the results of simulation studies of the dynamical behavior of lattice-model chains of from 25 to 100 beads, at concentrations ranging from very dilute to near melt, and exhibit the dependence of relaxation times upon chain length and concentration.

### MODEL

In our simulation, the face-centred-cubic lattice model<sup>5</sup> is adopted. The identical chains each consisting of  $N$  beads ( $N-1$  steps) are placed on a face-centred-cubic lattice. The simulation box with periodic boundary condition ( $20 \times 20 \times 20$ ) are employed, Brownian motion of the chain is simulated by choosing a piece of a chain at random and then moving only this piece of this chain according to rules which maintain chain connectivity. Entanglement and excluded volume effects are introduced by not allowing beads to move to

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sites which are already occupied. The model has been described in detail previously.<sup>5</sup> From time to time the coordinates of all the beads are sampled and recorded for later data analysis. The time scale for all simulations is taken to be equal to the total number of beads in the periodic system. If there are  $n$  chains in the periodic system, a single time step is taken to be  $nN$  attempted moves.

To analyze the dynamics of the chain, we use the values of the end-to-end vector,  $\mathbf{R}(t)$ , to compute the autocorrelation function,  $\rho_R(t)$ , defined by

$$\rho_R(t) = \langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle / \langle R^2 \rangle \quad (1)$$

where the broken brackets represent an equilibrium ensemble average. The relaxation time,  $T_R$ , is estimated by fitting an unweighted least-squares line to the linear, long-time region of a semilog plot of  $\rho_R(t)$  vs. time. The inverse of the relaxation time is the negative of the slope of the line. To analyze the dynamics in more detail, we also study the relaxation of the first three normal modes. The normal modes  $U_k(t)$  are given by the Rouse formula<sup>14</sup>

$$U_k(t) = \sum_{j=1}^N ((2 - \delta_{k0})/N)^{1/2} \times \cos\left(\left(j - \frac{1}{2}\right)\pi k/N\right) \mathbf{R}_j(t) \quad (2)$$

where  $\mathbf{R}_j(t)$  is the position of the  $j$ -th bead at time  $t$ . The autocorrelation function of the  $k$ -th normal mode,  $\rho_k(t)$ , is given by

$$\rho_k(t) = \langle U_k(t) \cdot U_k(0) \rangle / \langle U_k^2 \rangle \quad (3)$$

The relaxation time of the  $k$ -th mode,  $T_k$ , is computed by fitting a least-squares line to a semilog plot of  $\rho_k(t)$  vs. time. The negative of the relaxation time is the inverse of the slope of this line.

## RESULTS AND DISCUSSION

Simulations are carried out for chains of 25, 50, and 100 beads. For all but the 100-bead

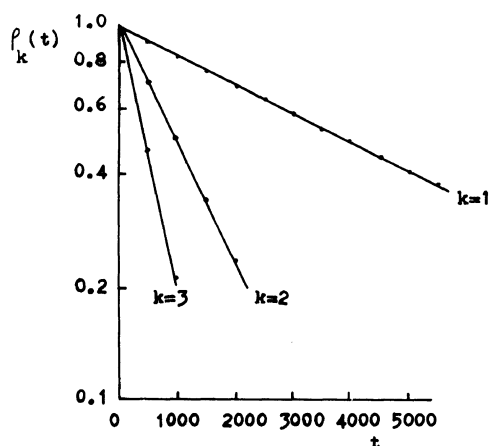


Figure 1. Semilogarithmic plot of autocorrelation functions  $\rho_k(t)$  vs. time  $t$  for the system of the chain of  $N=50$  beads occupying fraction  $c=0.50$ .

chains, simulations are carried out at seven values of the bead volume fraction  $c$ , defined as the fraction of lattice sites occupied by beads. The numbers of chains are chosen to give values of  $c$  spanning the range from 0.125 to 0.875. For the 100-bead chains, systems are studied at four values of  $c$ , from 0.125 to 0.50. Figure 1 shows semilogarithmic plot of the autocorrelation function  $\rho_k(t)$  vs. time  $t$  for the system of the chains of  $N=50$  beads occupying fractions  $c=0.50$ . The relaxation time of the  $k$ -th mode,  $T_k$ , are calculated by fitting an unweighted least-squares line to the curves. We also find end-to-end vector autocorrelation function  $\rho_k(t)$  is a single exponential at long times. For example, the long time range is from 1500 to 5000 for  $c=0.50$  and  $N=50$ . The relaxation time,  $T_R$ , is calculated from the long-time slopes of the  $\ln \rho_k(t)$  vs.  $t$  plot. The numerical values of relaxation times are collected in Table I. For  $c=0.0$  (the approximate case), the relaxation times of the isolated chains are also given in Table I. We find that relaxation times may be determined by

$$\begin{aligned} T_{R0} &= (N-1)^{\alpha_R(0)} \\ T_{k0} &= (N-1)^{\alpha_k(0)} \end{aligned} \quad (4)$$

where  $T_{R0}$  and  $T_{k0}$  are the relaxation times of

**Table I.** Values of relaxation times as a function of chain length  $N$ , and concentration  $c$ 

$c$		$N=25$		$N=50$		$N=100$	
		a	b	a	b	a	b
0.0	$T_R$	282		1370		7000	
	$T_1$	281		1370		7010	
	$T_2$	62.3		331		1670	
	$T_3$	26.3		137		730	
0.125	$T_R$	336	338	1700	1670	8600	8530
	$T_1$	340	337	1710	1680	8680	8600
	$T_2$	75.8	74.8	415	403	2030	2070
	$T_3$	31.8	31.5	167	167	866	906
0.25	$T_R$	430	418	2060	2100	10800	11200
	$T_1$	420	417	2130	2110	11800	11200
	$T_2$	91.0	92.4	517	507	2600	2660
	$T_3$	39.6	39.0	217	210	1080	1160
0.375	$T_R$	529	527	2700	2750	14100	15000
	$T_1$	523	535	2730	2740	14600	15000
	$T_2$	121	119	637	664	3310	3580
	$T_3$	50.1	51.9	286	295	1540	1560
0.50	$T_R$	728	728	3900	3820	21000	21500
	$T_1$	716	726	3980	3850	21900	21500
	$T_2$	160	161	927	923	4800	5130
	$T_3$	69.3	68.0	389	382	2100	2240

		$N=25$		$N=50$	
		a	b	a	b
0.625	$T_R$	1030	1080	6090	5850
	$T_1$	1010	1080	6100	5890
	$T_2$	230	239	1450	1410
	$T_3$	106	101	565	585
0.75	$T_R$	1910	1870	11000	10600
	$T_1$	1800	1880	10900	10700
	$T_2$	431	416	2620	2580
	$T_3$	170	176	1010	1070
0.875	$T_R$	4910	4860	32100	29800
	$T_1$	4890	4850	31200	30000
	$T_2$	1160	1080	7600	7190
	$T_3$	478	454	3100	2970

<sup>a</sup> Monte Carlo simulation.

<sup>b</sup> Values of eq 5, where  $\gamma_{R25} = \gamma_{k25} = 1.37$ ,  $\gamma_{R50} = \gamma_{k50} = 1.48$ , and  $\gamma_{R100} = \gamma_{k100} = 1.62$ .

the isolated chains. The values of  $\alpha_R(0)$  and  $\alpha_k(0)$  are determined by making plots of  $\ln T_R$  vs.  $\ln(N-1)$  and  $\ln T_k$  vs.  $\ln(N-1)$  respectively, and the results are  $\alpha_R(0) = 2.27$ ,  $\alpha_1(0) = 2.27$ ,  $\alpha_2(0) = 2.29$ , and  $\alpha_3(0) = 2.27$ . In Table I, relaxation times increase with increasing  $c$ .

Relaxation times are close to  $\infty$  when  $c = 1.0$  because no bead volume is permitted to move. Relaxation times may depend on the bead free volume  $(1-c)$ . We plot  $\ln T_R$  vs.  $\ln(1-c)$  and  $\ln T_k$  vs.  $\ln(1-c)$  at constant  $N$ , and find relaxation times are well described by the

relationship

$$\begin{aligned} T_R &= T_{R0}/(1-c)^{\gamma_{RN}} \\ T_k &= T_{k0}/(1-c)^{\gamma_{kN}} \end{aligned} \quad (5)$$

The values  $\gamma_{RN}$  and  $\gamma_{kN}$  are nearly the same for various  $k$ , and only depend on the chain length,  $N$ . In our model, the values are  $\gamma_{R25} = \gamma_{k25} = 1.37$ ,  $\gamma_{R50} = \gamma_{k50} = 1.48$ , and  $\gamma_{R100} = \gamma_{k100} = 1.62$  (for  $k=1, 2$ , and  $3$ ). The values of  $T_R$  and  $T_k$  from eq 5 are also listed in Table I. It is found that the maximum deviation from the results of Monte Carlo simulation is only 7.0%. Since the scaling exponents  $\gamma_{RN}$  and  $\gamma_{kN}$  increase with increasing  $N$ , relaxation times from eq 5 show deviations from the the Rouse theory,  $T \sim (N-1)^{2.2}$ , at high concentrations. For small  $c$ , the deviations are significant. This means that the Rouse theory is described for the short nonentangled system, and this result is agreement with previous simulation.<sup>9-13</sup>

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