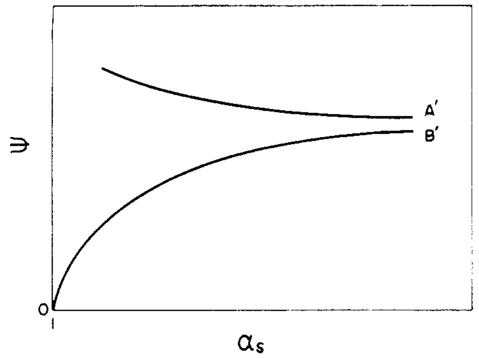

Figure 2. Schematic representation of Ψ vs. α_S plots for a linear flexible polymer in a good solvent: line A′, from eq 9 and 10; line B′, from two-parameter or renormalization-group theories.

elaborate renormalization-group methods.[6,7] Except for a calculation by Gobush et al.,[8] the proposed theories predict in common that Ψ is a universal function of α_S which starts from zero at $\alpha_S = 1$ and *increases* monotonically to a certain limiting value with an increase in α_S, as schematically shown by line B′ in Figure 2; Gobush et al.'s calculation shows Ψ to decrease with increasing α_S after passing through a broad maximum at $\alpha_S \sim 1.5$.

What is important in Figure 2 is the opposite curvatures of lines A′ and B′. This discrepancy indicates that any current A_2 theories except Gobush et al.'s are inconsistent with the above-mentioned experimental findings on linear flexible polymers in good solvents. Though quite serious, it does not seem to have been pointed out in previous publications.

Douglas and Freed[9] attributed the observed decreases in Ψ at large α_S to increasing polydispersity of the polymer samples of higher molecular weight and also to the improper account of the third virial coefficient in determining A_2 from light scattering data. However, as can be understood from the above analysis, it is legitimate to interpret the observed fact as the consequence of the convex-downward curvature of measured log A_2 vs. log M plots (see Figure 1). It can be shown that if line B' in Figure 2 holds for a linear flexible polymer in a good solvent, we should observe for such a system a log A_2 vs. log M plot of the type illustrated by line B in Figure 1a. However, as noted above, no actual data consistent with the curvature of this line have ever been reported.

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Communications to the Editor

Concentration Dependence of the Diffusion Coefficient and the Longest Relaxation Time of Polymer Chains in Solution

The concentration dependence of the long-time dynamical behavior of polymer chains as measured by the diffusion constant D and the longest relaxation time τ_1 provides an insightful means of examining the effect of inter- and intrachain interactions in concentrated polymer solutions and melts and of testing theoretical representations of these interactions and the physical models upon which they are built. The effect of the volume occupied by the chain and the resulting entanglement of the chain with itself and with other chains on dynamical behavior have been difficult to treat theoretically and to characterize experimentally. The Doi–Edwards[1] and de Gennes[2] models of concentrated polymer systems view the segmental motion of entangled chains as reptation of the polymer chain along its contour within a "tube" formed by neighboring chains. As pointed out by Wesson, Noh, Kitano, and Yu[3] (hereafter WNKY), the Doi–Edwards model predicts that D lacks a simple power-law dependence upon concentration c. Scaling laws as developed by de Gennes provide another theoretical approach to the concentration dependence of D, which is predicted to be the -1.75 power in a good solvent and the -3 power in a Θ-solvent or its concentration equivalent. Both of these approaches invoke several concentration regions with different predicted behavior.

In the experimental area, it has been equally difficult to characterize the concentration dependence of dynamical behavior. Recently, WNKY have reported[3] measurements of D as a function of concentration for labeled polystyrenes with molecular weights from 32 000 to 360 000. They examined their data in the context of the Doi–Edwards theory and scaling predictions and found that their results did not fit the predictions of the Doi–Edwards theory as formulated by Graessley.[4] Nor did they find the simple power-law dependences of D on c over wide concentration ranges predicted by scaling theory. Their results showed a power-law dependence of D upon c which became greater than -1.75 at weight fractions greater than 0.2 and approached -13 at the highest concentration studied. Overall they reported that the concentration profile of D was best represented as a smooth curve.

Recent NMR studies by von Meerwall, Amis, and Ferry[5] (hereafter MAF) on diffusion in polystyrene solutions showed similar results. They measured the diffusion constant of polystyrene from a concentration below overlap to concentrations above the onset of entanglement and again failed to observe the power-law dependences of D upon c predicted by scaling laws. However, if the concentration dependence of D due to free volume was factored out, the remaining concentration dependence appeared to agree with scaling theory at sufficiently high concentrations.

At the same time that WNKY reported their findings, we reported the results of Monte Carlo simulations of the dynamic and equilibrium properties of many-chain systems.[6] The concentration dependence of the long-time relaxation behavior of our lattice models is represented reasonably well by a simple free volume model and an

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additional chain-length dependent factor. In the present paper we compare the concentration dependence of D and τ_1 for our lattice models with the data reported in ref 3 and 5 and with the theoretical predictions. We also compare our results with a recent suggestion by Nemoto, Landry, Noh, Kitano, Wesson, and Yu[7] (hereafter NLNKWY) that the concentration dependence of the diffusion constant can be factored into three parts: a free-volume part, independent of molecular weight M; a simple M^{-2} molecular weight dependence; and a non-free-volume factor independent of molecular weight. NLNKWY suggest that the power-law dependence of this last factor upon concentration may agree with scaling predictions.

The dynamical lattice model of a collection of linear polymer chains used in the multichain simulation is described elsewhere.[6] Briefly, each chain is modeled by a set of N connected points, which we refer to as beads, on a simple cubic lattice, the connections lying along cube edges. Brownian motion of the chains is simulated by repeated application of an elementary move process which consists of choosing a piece of one chain at random and then moving only this piece according to rules which maintain chain connectivity. Entanglement and excluded volume effects are introduced by not allowing beads to move to lattice sites which are already occupied. Deutch and coworkers have suggested[8] that the use of only one kind of elementary move process in earlier simulations of this sort led to artificial lengthening of the long relaxation times for chains with excluded volume. The use of a random mixture of two kinds of elementary move processes would eliminate the constraint which was essential to Deutch's argument. A subsequent study[9] showed that the apparent lengthening of the time scales introduced by excluded volume was indeed reduced, but by no means eliminated, by the use of two kinds of elementary move processes. Consequently, all our subsequent simulations of chains with excluded volume have employed a random mixture of two kinds of elementary bead move processes.[10]

As the simulation proceeds, at intervals the state of the system is examined and chain dimensions, autocorrelation function values, and center-of-mass locations are sampled for the eventual estimation of mean-square end-to-end lengths $\langle l^2 \rangle$, long relaxation times τ_1, and translational diffusion constants D, respectively. Since the time intervals over which center-of-mass displacements were sampled were too short in some cases for the resulting values of D to be altogether trustworthy, we here examine the behavior both of D and of the ratio $\langle l^2 \rangle/\tau_1$, which is proportional to D for Rouse-model chains.

Log-log plots, shown in Figure 1, of D and $\langle l^2 \rangle/\tau_1$ vs. the fraction ϕ of occupied lattice sites show large changes in slope qualitatively similar to those observed experimentally by WNKY using forced Rayleigh scattering and by MAF using spin-echo NMR. In agreement with the experimental studies, there is no evidence in our simulation results for a unique power-law dependence of D or $\langle l^2 \rangle/\tau_1$ upon ϕ over a wide range of concentration.

Figure 1 also shows that the concentration dependence of D is very similar to that of $\langle l^2 \rangle/\tau_1$. We therefore choose to examine the concentration dependence of the latter quantity, which is not subject to uncertainties regarding sampling-time intervals. In ref 6 we showed that the values of τ_1 obtained for the lattice models were reasonably well fitted by the form

$$\tau_1(N,\phi) = \tau_1(N,0) \exp[0.46\phi/(1-\phi)]N^{0.56\phi} \qquad (1)$$

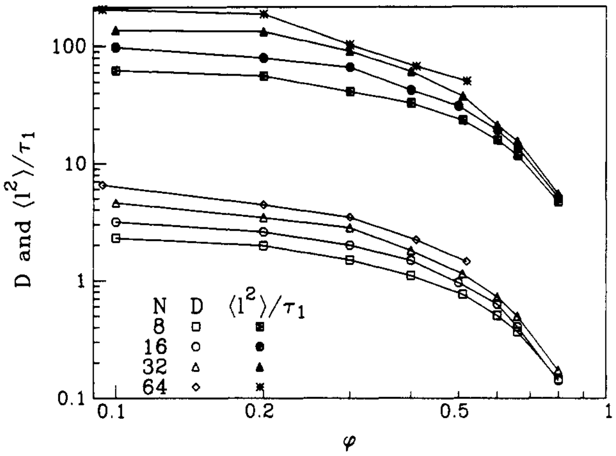

Figure 1. Log–log plots of diffusion constants D and ratios $\langle l^2 \rangle/\tau_1$ of mean-square end-to-end length $\langle l^2 \rangle$ to long relaxation time τ_1 vs. fraction ϕ of occupied lattice sites for sets of chains of N beads each on a simple cubic lattice.

Table I
Logarithmic Derivatives S_T = d ln($\langle l^2 \rangle/\tau_1$)/d ln ϕ of the Ratio of Mean-Square End-to-End Length $\langle l^2 \rangle$ to Long Relaxation Time τ_1 with Respect to the Fraction ϕ of Occupied Lattice Sites for Sets of Chains of N Beads Each Calculated from Eq 3, and the Free-Volume S_F and Remaining S_R Contributions to S_T ($S_T = S_F + S_R$)

N	ϕ	S_T	S_F	S_R
8	0.1	−0.18	−0.06	−0.12
8	0.2	−0.39	−0.14	−0.25
8	0.3	−0.66	−0.28	−0.37
8	0.4	−1.01	−0.51	−0.50
8	0.5	−1.54	−0.92	−0.62
8	0.6	−2.47	−1.73	−0.75
8	0.7	−4.45	−3.58	−0.87
8	0.8	−10.20	−9.20	−1.00
16	0.1	−0.23	−0.06	−0.18
16	0.2	−0.50	−0.14	−0.35
16	0.3	−0.81	−0.28	−0.53
16	0.4	−1.22	−0.51	−0.71
16	0.5	−1.81	−0.92	−0.89
16	0.6	−2.79	−1.73	−1.06
16	0.7	−4.82	−3.58	−1.24
16	0.8	−10.62	−9.20	−1.42
32	0.1	−0.29	−0.06	−0.23
32	0.2	−0.60	−0.14	−0.46
32	0.3	−0.97	−0.28	−0.69
32	0.4	−1.43	−0.51	−0.92
32	0.5	−2.06	−0.92	−1.14
32	0.6	−3.10	−1.73	−1.37
32	0.7	−5.18	−3.58	−1.60
32	0.8	−11.03	−9.20	−1.83
64	0.1	−0.34	−0.06	−0.28
64	0.2	−0.70	−0.14	−0.56
64	0.3	−1.12	−0.28	−0.84
64	0.4	−1.63	−0.51	−1.12
64	0.5	−2.32	−0.92	−1.40

We find that the values of $\langle l^2 \rangle$ in ref 6 appear to be fitted reasonably well by the form

$$\ln \langle l^2 \rangle = a + b\phi + (c + d\phi) \ln (N-1) \qquad (2)$$

A linear least-squares fit to the form of eq 2 yields the values $a = 0.072$, $b = 0.27$, $c = 1.19$, and $d = -0.18$. Using these values and those in eq 1, we obtain

$$\mathrm{d} \ln (\langle l^2 \rangle/\tau_1)/\mathrm{d} \ln \phi = S_F + S_R \qquad (3)$$

where

$$S_F = -0.46\phi/(1-\phi)^2$$

and

$$S_R = \phi[0.27 - 0.18 \ln (N-1) - 0.56 \ln N]$$

Here, S_F is the free-volume contribution and S_R the remaining contributions to the concentration dependence. These two terms and their sum are shown in Table I and confirm the smooth variation of concentration dependence and the lack of unique power-law dependences over significant ranges of concentration. Over the range of values of N and ϕ studied in this work, the power-law dependence goes from −0.18 to −11. At the highest concentrations, where the power-law dependence is greatest, it will be seen that the major contribution comes from the free-volume term S_F. The non-free-volume term S_R is proportional to ϕ and clearly cannot remain even approximately constant over significant ranges of ϕ. We further note that the non-free-volume term S_R is not independent of N as would be required by the suggestion of NLNKWY.

In summary, the simulation results, like the experimental results of WNKY and MAF, exhibit a wide range of power-law dependence of D upon concentration and a complete absence of regions of constant power-law dependence. Further, the concentration dependence of D appears to be dominated by local free volume, as is also suggested by the experimental results of MAF. However, the non-free-volume term fails to exhibit the region of constant (−1.75) power-law dependence observed in the analysis of MAF and is not independent of molecular weight as suggested by NLNKWY.

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CORRECTIONS

Brigitte Albert, Robert Jérôme, Philippe Teyssié, Gerard Smyth, Noel G. Boyle, and Vincent J. McBrierty*: Investigation of Compatibility in Syndiotactic Poly(methyl methacrylate)/Poly(vinyl chloride) Blends. Volume 18, Number 3, March 1985, p 388.

Figure 1 of this paper incorrectly portrays the T_1 data for the 60/40 s-PMMA/PVC blend. The correct figure is presented herein.