Macromolecules **1995,** *28,* 4747−4749 **4747**

End-to-End Vector Correlation Function in Many-Chain Systems

Juan J. Freire*

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

Keiichiro Adachi

Department of Macromolecular Sciences, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Received November 30, 1994
Revised Manuscript Received March 20, 1995

The dynamic properties of polymer chains can be studied through different simulation techniques. Thus, molecular dynamics (MD) or Brownian dynamics (BD) algorithms involve the calculation of dynamic trajectories, obtained by solving deterministic (MD) or stochastic (BD) equations of motion. Moreover, Monte Carlo (MC) simulations also serve to obtain trajectories, but only when one assumes that the Markovian process employed to generate new configurations from the previous ones (MC bead−jumps or moves) is a realistic representation of the system, in a given time scale associated with the stochastic process.[1,2] Dynamic MC algorithms have been designed with different combinations of rules[3,4] for the moves, and the results obtained with these methods have been carefully compared with predictions based on theoretical models for the dynamics of flexible chains. In particular, the MC methods have been shown to reproduce the scaling laws for the diffusion coefficient and the first (longest) internal modes of isolated chains[5,6] versus the chain length (or molecular weight) predicted by the Rouse theory.[7] Moreover, long dynamic MC trajectories have been obtained with the purpose of elucidating the dynamics of many-chain systems,[8,9] for which the MC techniques are particularly efficient. However, due to the somewhat artificial nature of the basic motions involved in the dynamic MC trajectories, it is desirable to analyze their capability to mimic as many dynamic properties as possible. In particular, the direct comparison of MC results with experimental data of complex properties can constitute an excellent test of the method. In some cases, where existing theory cannot reproduce the experimental behavior, the Monte Carlo data are also useful to provide a physical explanation of these data. With these aims in mind, we present in this work a comparison of the Rouse theory, with MC results for the end-to-end vector time correlation function,[6,10] obtained in previous work,[11] and also with previously obtained experimental data[12−14] for dielectric relaxation, in both the dilute and nondilute polymer regimes.

The MC simulations and experimental measurements were performed in separate investigations involving the present authors. The MC trajectories[11] were obtained by means of a bead−jump algorithm including inner or end local motions, as bends and crankshafts, for self-avoiding chains in a cubic lattice. The time unit is defined as MC step, i.e., a number of tried MC moves equal to the total number of polymer units in the system. The resulting trajectories were analyzed to obtain different dynamic properties. We will only mention here the time correlation functions corresponding to the first three Rouse modes of a chain of N beads, defined as

$$\varrho_k(t) = \langle \mathbf{u}_k(0)\cdot\mathbf{u}_k(t)\rangle / \langle \mathbf{u}_k^{\,2}\rangle,\ k = 1, 2, 3 \qquad (1)$$

where

$$\mathbf{u}_k(t) = (2/N)^{1/2}\sum_{i=1}^{N}\cos[(i - {}^1\!/_2)\pi k/N]\mathbf{R}_i \qquad (2)$$

where $\mathbf{R}_i(t)$ is the position vector of bead i, referred to the first bead. From the time correlation functions, assuming a single-exponential behavior consistent with the Rouse theory, the relaxation times τ_k were obtained as

$$\varrho_k(t) \sim \mathrm{e}^{-t/\tau_k} \qquad (3)$$

(Results for the first three relaxation times of different systems were reported in ref 11.)

The correlation function $\varrho_k(t)$ of the end-to-end vector was also obtained[11] as

$$\varrho_{\mathrm{R}}(t) = \langle \mathbf{R}(0)\cdot\mathbf{R}(t)\rangle / \langle \mathbf{R}^2\rangle \qquad (4)$$

This function was characterized by means of a relaxation time, τ_{R}, whose value was very similar to τ_1. However, the fit to a single-exponential was only adequate in this case for the long time range, since the results showed a clear curvature at short times.

In fact, according to the Rouse theory, $\varrho_{\mathrm{R}}(t)$ has contributions of different internal modes. Thus, it can be shown[12] that

$$\varrho_{\mathrm{R}}(t) = (8/\pi^2)\sum_{k=\mathrm{odd}}^{N}(1/k^2)\mathrm{e}^{-t/\tau_k} \qquad (5)$$

where

$$\tau_k = N^2 b^2 \xi / (3 k_{\mathrm{B}} T \pi^2 k^2) \qquad (6)$$

ξ is the bead friction coefficient, b is the bead statistical length, and $k_{\mathrm{B}}T$ is the Boltzmann factor. The MC results can be compared with this theoretical formula if one introduces numerical values for the different τ_k in eq 5.

The dynamical MC methods involve the use of Monte Carlo time units, whose relation to real time scales can only be established with the help of a proportionality constant. Then eq 6 can only be compared with MC results in the form of the scaling law $\tau_k \sim N^2k^{-2}$. (This scaling law was confirmed in our previous analysis of the first three relaxation times of chains with different lengths at different concentrations.[11]) Therefore, one can incorporate eq 6 into eq 5 for a given system, by establishing that $\tau_k \sim k^{-2}$ for all the relaxation times and introducing one of the relaxation times obtained independently from the MC trajectories, according to eqs 1−3. For this purpose, we make use of the first relaxation times τ_1, since the accuracy in the determination of relaxation times decreases with increasing k. (A similar approach has also been employed in the comparison of the experimental dielectric relaxation data with the Rouse theory, as will be described below.)

In Figure 1 we show the comparison between our MC data for $\varrho_k(t)$ and the Rouse results obtained according

0024-9297/95/2228-4747$09.00/0

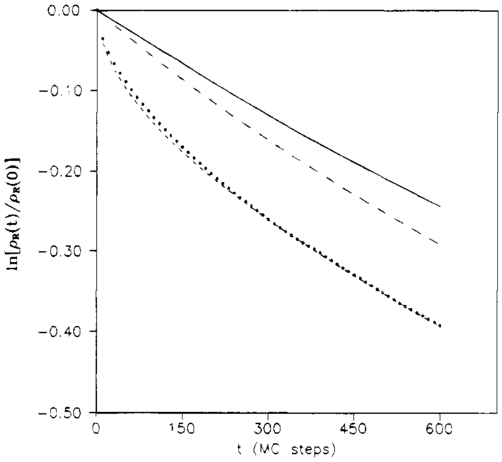

Figure 1. Normalized time-correlation function of the end-to-end vector for a single chain ($N = 84$). The circles represent MC data. The short-dashed line corresponds to the Rouse theory curve (eq 5). The long-dashed curve was obtained by truncating the eq 5 summation at $k = 3$. The solid line is the exponential decay obtained with the first relaxation time.

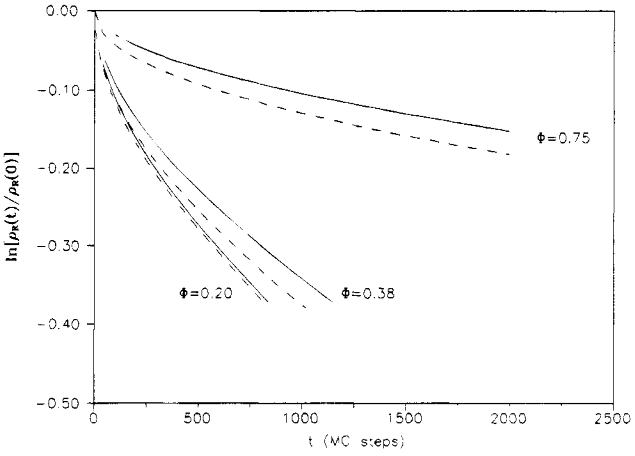

Figure 2. Normalized time-correlation function of the end-to-end vector of many-chain systems of $N = 84$ and the indicated concentrations. The solid line shows the Rouse prediction, from eq 5. The dashed line represents the MC data.

to eqs 5 and 6, for an isolated chain of 84 units. It can be observed that there is satisfactory agreement. A similar degree of agreement is obtained with other chain lengths ($N = 18, 36, 60$). We also show in Figure 1 the results obtained by truncating eq 5 at $k = 3$, i.e., considering only the contribution of two internal modes. This curve differs considerably from both the MC and the theoretical values, pointing out that the $\varrho_R(t)$ curve can only be reproduced by taking into account many internal modes. (The decay corresponding to the first relaxation time is also shown in Figure 1.) It should be remarked that, since the Rouse formula for $\varrho_R(t)$ involves many contributions, the present comparison can be considered as a severe test to confirm the capability of the dynamic Monte Carlo methods to reproduce the Rouse dynamics of a single chain.

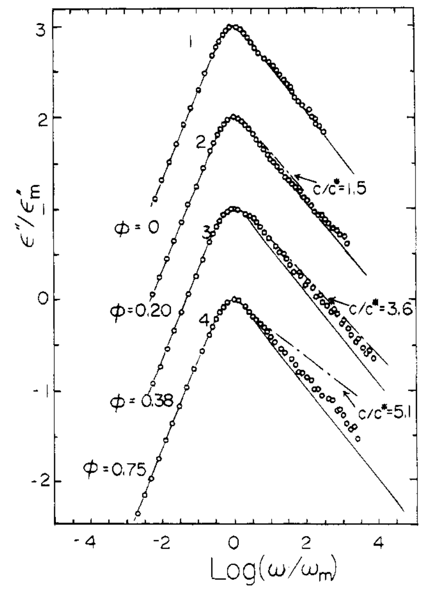

Figure 3. ϵ'' curves calculated for chains of $N = 84$ and the indicated concentrations ($\Phi = 0$ denotes a single-chain system). The solid lines represent the Rouse theory predictions and the dash-dotted lines correspond to experimental ϵ'' curves for PI/Hep solutions with given values of c/c^*. The circles are points obtained from the MC data of the time-correlation functions.

In Figure 2 we show the results obtained for more concentrated systems ($N = 84$). We present curves corresponding to different values of the polymer fraction, Φ. It can be verified that the agreement between the Rouse theory and the MC data is still reasonable for $\Phi = 0.20$, but the MC curves exhibit a more pronounced curvature and a faster initial decrease when the concentration is higher. Our estimation of the critical concentration, Φ^*, for which chains overlap is $\Phi^* \cong 0.10$ for $N = 84$ (this estimation is slightly smaller than the one used for the previous discussion of the MC data in ref 11). It can be noticed that the differences between MC and Rouse results appear at concentrations significantly higher than Φ^* for $N = 84$ (and a similar behavior is found for shorter chains).

Finally we compare the MC simulations with experimental data of the dielectric normal-mode relaxation for solutions of polyisoprene (PI) which possesses the dipole moment aligned in the direction parallel to the chain contour.[13,14] The complex dielectric constant ϵ^* ($\equiv \epsilon' - i\epsilon''$) for such a polymer is given by the Fourier transform of the time derivative of the correlation function $\varrho_R(t)$:

$$\epsilon^* - \epsilon_\infty = -\Delta\epsilon \int_0^\infty (\mathrm{d}\varrho_R(t)/\mathrm{d}t) \exp(-i\omega t)\, \mathrm{d}t \qquad (7)$$

where ϵ_∞ is the high-frequency dielectric constant, $\Delta\epsilon$ the dielectric relaxation strength, and ω the angular frequency. The data of $\varrho_R(t)$ for the chain of $N = 84$ with $\Phi = 0, 0.20, 0.38$, and 0.75 have been transformed into the dielectric loss factor ϵ'' according to eq 7. In order to compare the shapes of different ϵ'' curves, we have normalized ϵ'' with its maximum value ϵ_m''. These normalized data are plotted against ω/ω_m in Figure 3 where ω_m denotes the maximum loss frequency. In Figure 3, the solid and dashed curves respectively show the normalized ϵ'' curve calculated with the Rouse theory and normalized experimental data of PI ($M_W = 743\,000$) solutions[14] in heptane (Hep) with c/c^* similar to the ratios Φ/Φ^* employed in the simulations (c and c^* denote the concentration and the overlapping concentration in units of g/cm^3). It can be observed that the ϵ'' curve calculated from the MC data for $\Phi \cong 0$ agrees with the Rouse theory, but the curves corresponding to the range $\Phi > \Phi^*$ broaden for $\omega/\omega_m > 1$. This feature is expected from the direct analysis of the correlation functions and is qualitatively consistent with the experimental results: the ϵ'' curves for dilute PI/Hep solutions agree with the Rouse theory, but they broaden[14] in the concentration range from c^* to $10c^*$. An increase of c above $10c^*$ does not produce any further broadening of the experimental curves. It should be noted that the tube model proposed by de Gennes[15] cannot explain the present results, since this theory predicts the same model distribution as the Rouse theory (eq 5).

In Figure 3 we observe that the ϵ'' curves obtained from MC data at $\Phi = 0.20$ and 0.38 agree fairly well with the experimental curves, but at $\Phi = 0.75$ the MC curve is narrower than the experimental data. A possible explanation for the difference in shape between these curves based in MC and experimental data is the relatively small size of the simulated chains ($N = 84$) which is not high enough to simulate the dynamics of a fully entangled system. It should be also considered that the MC data for $\Phi = 0.75$ exhibit higher uncertainties, though we do not believe that an extensive computation for this case, in order to eliminate the apparent noise in the data, would result in a noticeable broadening. In spite of these problems, we have successfully demonstrated that many-chain systems certainly exhibit a dynamics which cannot be described by the Rouse theory.

Acknowledgment. This work has been supported in part by Grant PB92-0227 from the DGICYT (J.J.F.).

References and Notes

(1) Binder, K. In *Molecular Level Calculations of the Structures and Properties of Non-Crystalline Polymers*; Bicerano, J., Ed.; Marcel Dekker: New York, 1989.
(2) Verdier, P. H. *J. Chem. Phys.* **1966**, *45*, 2118.
(3) Boots, H.; Deutch, J. M. *J. Chem. Phys.* **1977**, *67*, 4608.
(4) Verdier, P. H. *J. Chem. Phys.* **1970**, *52*, 5512; **1973**, *59*, 6119.
(5) Kranbuehl, D. E.; Verdier, P. H. *Macromolecules* **1984**, *17*, 749.
(6) Crabb, C. C.; Kovac, J. *Macromolecules* **1985**, *18*, 1430.
(7) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(8) Kremer, K. *Macromolecules* **1983**, *16*, 1632.
(9) Skolnick, J.; Kolinski, A. *Adv. Chem. Phys.* **1990**, *78*, 223.
(10) Verdier, P. H.; Kranbuehl, D. E. *Macromolecules* **1987**, *20*, 1362.
(11) López Rodriguez, A.; Rey, A.; Freire, J. J. *Macromolecules* **1992**, *25*, 3266.
(12) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(13) Adachi, K.; Kotaka, T. *Prog. Polym. Sci.* **1993**, *18*, 585.
(14) Urakawa, O.; Adachi, K.; Kotaka, T. *Macromolecules* **1993**, *26*, 2042.
(15) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.

MA946258P