Relaxation of a Single Chain Molecule in Good Solvent Conditions by Molecular-Dynamics Simulation

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The dynamic relaxation of various structural properties of a single freely jointed N-mer ($N=6,9,30$) in explicit solvent at relatively high dilution is investigated by molecular dynamics. In the large-k region, the normalized intermediate scattering function $I(k,t)$ appears to be a universal function of tk^x with $x=2.9\pm0.1$, in good agreement with experiments and close to the prediction of the Zimm model ($x=3$).

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Most of the computer-simulation studies of the dynamic relaxation of polymers in dilute solution have been restricted to models treating the environment of the chain in a stochastic way. Various dynamic Monte Carlo or "Brownian dynamics" schemes have been exploited either in continuum[1-3] or on lattices.[4] Full "atomic" models of solvent have been the object of a few molecular-dynamics (MD) studies,[5-8] which, in comparison with the results of the "cheaper" stochastic methods, have been much less conclusive about the validity of dynamic scaling laws.

In the present Letter, we report MD simulation results for various systems consisting of one N-mer ($N=6$, 9, or 30) embedded in a Lennard-Jones solvent at fixed temperature and density corresponding to good solvent conditions. Our main result concerns the universal behavior of the intermediate scattering function $S(k,t)$ of the chain in the accessible "high" k region, typically $2\pi/d > k > 2\pi/R_g$, where d is the bond length between adjacent monomers and R_g is the gyration radius of the chain. A single curve is obtained for all N-mers when $I(k,t)=S(k,t)/S(k,0)$ is plotted as a function of the renormalized time $t'=t(kd)^x$ with $x=2.9\pm0.1$. This result is in remarkable agreement with light-scattering experimental data on polystyrene in benzene[9] which yield $x^{\text{expt}}=2.85\pm0.05$. Scaling theory[10,11] relates x to two other scaling exponents ν and ν', defined by $R_g \propto (N-1)^\nu$ and by the center-of-mass diffusion coefficient $D_G \propto (N-1)^{-\nu'}$, through $x=2+\nu'/\nu$ and $\nu=0.6$ for chains in good solvent conditions. In the presence (Zimm model) or in the absence (Rouse model) of hydrodynamic interactions,[10,11] the exponents are predicted to be $\nu'=\nu$, $x=3$ and $\nu'=1$, $x=\frac{11}{3}$, respectively. To our knowledge, our estimate of x is the first computer-simulation evidence of a Zimm-type relaxation, in contrast with the above-mentioned stochastic simulations which, quite consistently with the absence of explicit solvent, led systematically to Rouse-type relaxation.

We have also studied the dynamic relaxation of various structural quantities such as the end-to-end vector $\mathbf{R}$, its square modulus R^2, and R_g^2. The two last quantities show, within statistical errors, the same relaxation behavior. For $\mathbf{R}$ and R^2, single curves are obtained for different chain sizes in terms of a renormalized time $t/(N-1)^\alpha$, where α is close to 1.55 for both quantities (see Table II). This suggests that the natural time scale for those quantities is somewhat different from that for $S(k,t)$ in the large-k regime, the latter being $\alpha=\nu x=1.69\pm0.06$.

According to scaling arguments,[10] the static structure factor $S(k)$ should obey a power law $k^{-1/\nu}$ in the range $2.5/R_g \le k \le \pi/d$. This is indeed observed and yields $\nu=0.584\pm0.001$ for $N=30$. Assuming that our chains are already in the static scaling regime, the N dependence of R_g (see Table II) gives $\nu=0.568\pm0.006$ in fair agreement with the previous estimate.

Our experiments may be described as follows. The N beads of a freely jointed chain and the N_s solvent molecules have the same mass m. The same Lennard-Jones interaction (σ,ε), truncated and shifted to zero at its minimum, is imposed between any solvent-solvent, bead-solvent, or bead-bead pair except for first-neighbor beads along the chain which are connected by a rigid bond of length $d=1.075\sigma$. The equations of motion were integrated in Cartesian coordinates with the velocity version of the Verlet algorithm[12] using a time step $\Delta t=0.005\sigma(m/\varepsilon)^{1/2}$. The bond length was kept fixed by using the SHAKE iteration scheme.[13] In order to compare different systems in similar thermodynamic conditions, the density was always fixed to $\rho=(N+N_s)/V=0.80496\sigma^{-3}$ with a ratio N_s/N close to 23 (see Table I). We used periodic boundary conditions and generated the initial system configuration on a simple cubic lattice with a lattice constant equal to d. The imposed ratio N_s/N then led us to take, for two system sizes, a slightly noncubic MD box; however, we did not detect any anisotropy of the structure factor of the chain. The temperature was fixed to $k_BT/\varepsilon=1.5$ by a thermostat of the Nose-Hoover type[14] with an inertial "mass" parameter Q fixed by $Q/g=0.02m\sigma^2$, where $g=2N+1+3N_s-3$ is the total number of degrees of freedom coupled to the thermostat. For all systems, the pressure P was virtually the same, $P/\rho k_BT=7.35\pm0.01$. In Table I we report the time lengths of our experiments which are more than

TABLE I. End-to-end distance R, gyration radius R_g, and center-of-mass diffusion coefficient D_G for the chain lengths considered. $D_G(v)$ and $D_G(r)$ are the values estimated from the velocity autocorrelation function and from the mean-square displacement, respectively. N_s and N_t are the number of solvent particles and the number of time steps. τ_N is defined by $\tau_N = R_g^2/D_G$ and $\mathcal{T}$ denotes the time length of the run. Reduced units are defined as follows: $R = R^*\sigma$, $D_G = D_G^*\sigma(\varepsilon/m)^{1/2}$, $\tau_N = \tau_N^*\sigma(m/\varepsilon)^{1/2}$.

N	N_s	$10^{-6}N_t$	R^*	R_g^*	$10^2 D_G^*(v)$	$10^2 D_G^*(r)$	τ_N^*	$\mathcal{T}/\tau_N$
6	144	4	2.76 ± 0.02	1.165 ± 0.005	2.5 ± 0.1	2.430 ± 0.006	56	358
9	207	4	3.74 ± 0.04	1.525 ± 0.008	2.0 ± 0.1	1.96 ± 0.01	120	168
30	690	11	7.8 ± 0.1	3.16 ± 0.03	0.86 ± 0.05	0.818 ± 0.001	1220	45

1 order of magnitude longer than in previous similar studies.[5,7,8]

Table I also shows the measured values of R and R_g. When plotted against $N-1$, they obey power laws which provide estimates of the Flory exponent ν slightly below 0.6 (see Table II).

The structure factor $S(k)$ for all chain lengths is shown in Fig. 1 as a function of k. Even for the shortest chain ($N=6$), $S(k)$ presents a region in which it can be described by the power law $S(k) = C_N k^{-1/\nu}$. The estimated values of ν for different N are reported in Table II. Scaling arguments are founded on the assumption that for very long chains and for $kR_g \gg 1$ the constant C_N does not depend on the chain length.[10] Our results show that the power-law behavior in $S(k)$ is indeed observed in the expected k range, although $S(k)$ has, of course, not reached its N-independent limit. In the next discussion on dynamic scaling, ν will always be considered as a fixed parameter with a numerical value corresponding to the slope of $\ln S(k)$ for $N=30$ (see Table II).

The main object of this work was to analyze the relaxation of the chain in solution which is best characterized by the intermediate scattering function $S(k,t)$. For this quantity, the scaling hypothesis leads to the expression[15]

$$S(k,t) = NF(kR_g, R_g^{-2}D_G t)\,, \tag{1}$$

where F is a universal function. In the regime $kR_g \gg 1$ where internal motions of the chain are probed, $S(k,t)$ is expected to be independent of N. If, in addition, it is assumed that N is sufficiently large for R_g and D_G to depend on N as $R_g \propto N^{\nu}$ and $D_G \propto N^{-\nu'}$, $S(k,t)$ should be of the form

$$S(k,t) = N(kR_g)^{-1/\nu}\hat{F}(R_g^{-2}D_G t(kR_g)^x)\,, \tag{2}$$

with $x = 2 + \nu'/\nu$ for the argument of $\hat{F}$ to be independent of N. It implies that, in the above-mentioned regimes for N and k, $I(k,t) = S(k,t)/S(k,0)$ should be a universal function of the argument $R_g^{-2}D_G t(kR_g)^x$ for arbitrary chain size N and wave vector k.

In order to test these ideas, we computed an approximate inverse of $I = I(k,t)$ for $N=9$ and $N=30$ by selecting seven equally spaced values of I, ranging from 0.1 to 0.7, and measuring for all k curves the corresponding value of $t = t(k,I)$. The above universality demands that, for each I value, the product $t(k,I)k^x$ be independent of k and N. Figure 2 shows for $N=30$ a log-log plot of $t(k,I)$ vs k for all of those I values. The expected power law is indeed observed in the region $1 \le kd \le 4$. However, we detect a slight ($\pm 5\%$) but systematic dependence of the x exponent on I. By averaging over all slopes, we estimate the value $x = 2.9 \pm 0.1$ which turns out to be in remarkable agreement with the experimental value[9,11] $x = 2.85 \pm 0.05$. It should be noted that the curves $t(k,I)$ vs k for $N=9$ are in fair agreement with the $N=30$ case, but the dispersion on x is now doubled, suggesting that the universality should be, of course, more firmly established when longer chains are considered. Figure 3 shows $I(k,t)$ vs $t(k,I)k^{2.9}$: For each chain size, two values of k in the scaling region are shown. Given the statistical error on the exponent (not shown in the figure for sake of clarity) all curves are consistent.

This x value, being close to the theoretical prediction

TABLE II. Values of the static and dynamic exponents ν, α, and ν' estimated from different sources (see text).

Flory exponent			Dynamic exponents		
Source		ν	Source	α	ν'
R^2		0.591 ± 0.008	$S(k,t)$ ($N=30$)	1.69 ± 0.06	0.52 ± 0.02
R_g^2		0.568 ± 0.006	$C_{R^2}(t)$	1.56 ± 0.07	0.39 ± 0.02
$S(k)$	($N=6$)	0.587 ± 0.003	$C_{\mathbf{R}}(t)$	1.54 ± 0.03	0.37 ± 0.01
	($N=9$)	0.583 ± 0.002	$D_G(v)$	$\cdots$	0.62
	($N=30$)	0.584 ± 0.001	$D_G(r)$	$\cdots$	0.62

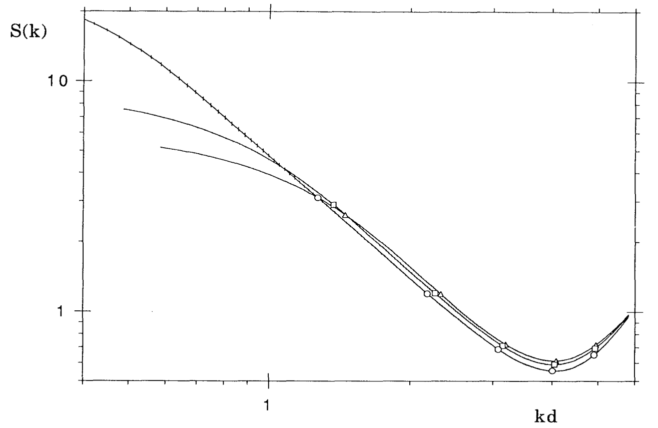

FIG. 1. Static structure factor $S(k)$ for different chain lengths: $N=30$ (○), 9 (□), and 6 (△).

of a Zimm-type relaxation[10] $x=3$, is a clear indication that the solvent does indeed play a fundamental role in the relaxation process. From the above theoretical analysis of $S(k,t)$, we can extract the diffusion-coefficient exponent $\nu'=\nu(x-2)=0.52\pm0.05$. This exponent is again very close to the experimental estimate[9] $\nu'=0.55\pm0.02$ based on diffusion-coefficient measurements through the small-k behavior of $S(k,t)$.

The most direct way to determine ν' in our simulation consists of measuring the slope of $\ln D_G$ against $\ln(N-1)$. Estimates of D_G obtained by integrating the velocity autocorrelation function and by measuring the slope of the mean-square displacement of the chain are reasonably consistent (see Table I). The existence of a power law for D_G is much less evident than for R_g: Although such a law cannot be ruled out, it is hard to make a definite statement at this stage. This is not in contradiction with theoretical arguments which predict the onset of the scaling regime for this quantity in a higher N region than for static properties.[15] Nevertheless, the best fit to the law $D_G \propto (N-1)^{-\nu'}$ yields a value of $\nu'=0.62$ which is not far from the value obtained in the $S(k,t)$ analysis.

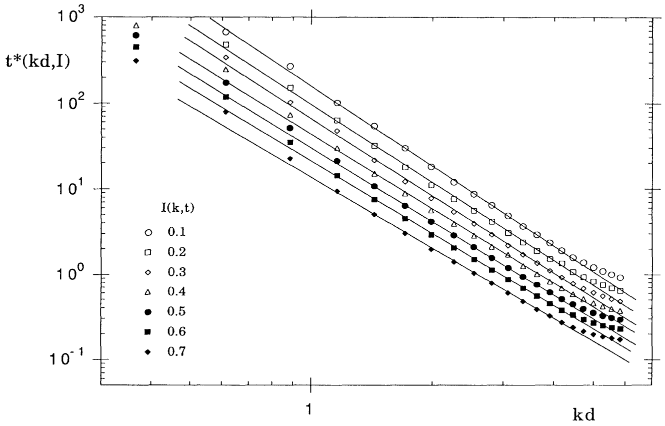

FIG. 2. $N=30$. Parametric plot of $t^*(kd,I)$ vs kd for all considered values of $I(k,t)=S(k,t)/S(k,0)$. The straight lines are power-law fits of the data in the region $1\leq kd\leq 4$. The estimated exponent x is ranging from 3.12 ($I=0.1$) to 2.77 ($I=0.7$). Reduced time is defined as $t=t^*\sigma(m/\varepsilon)^{1/2}$.

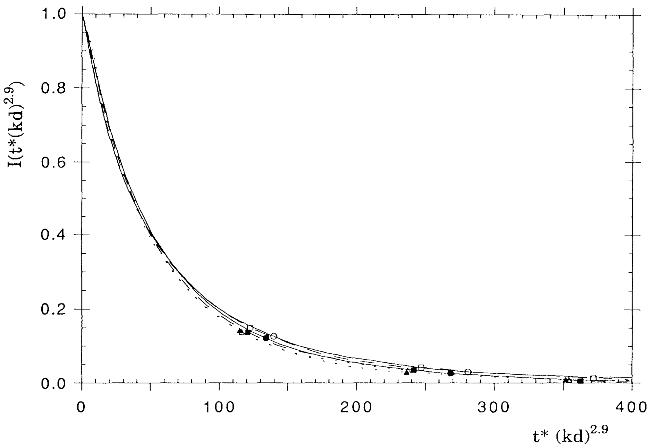

FIG. 3. Normalized intermediate scattering function $I(k,t)$ vs the rescaled independent variable $t^*(kd)^{2.9}$ for $N=30$ (solid line), 9 (long-dashed line), and 6 (short-dashed line). Two k values in the scaling region are shown for each N: $N=30$, $kR_g=6.3$ (○), $kR_g=11.4$ (●); $N=9$, $kR_g=3.9$ (□), $kR_g=5.2$ (■); $N=6$, $kR_g=4.0$ (△), $kR_g=4.7$ (▲). Reduced time is defined as $t=t^*\sigma(m/\varepsilon)^{1/2}$.

Relaxation of the chain conformation can also be monitored through normalized time correlation functions of R^2, R_g^2, and $\mathbf{R}$ defined for any chain property A as

$$C_A(t)=\frac{\langle A(t)A(0)\rangle-\langle A\rangle^2}{\langle A^2\rangle-\langle A\rangle^2}\,. \tag{3}$$

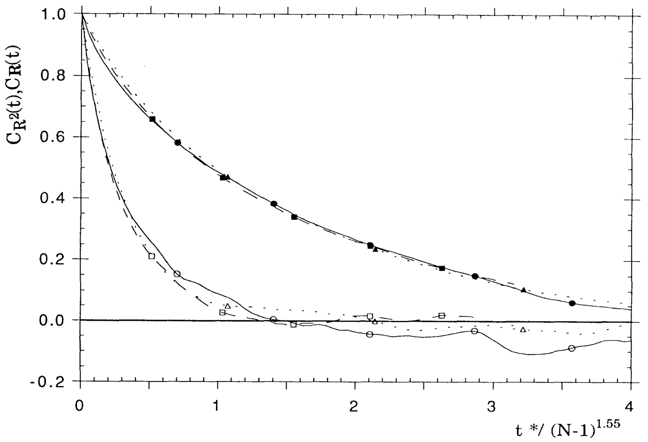

FIG. 4. Normalized time correlation functions of the square end-to-end distance C_{R^2} (open symbols) and the end-to-end vector $C_{\mathbf{R}}$ (solid symbols) vs the renormalized time $t^*/(N-1)^{1.55}$ for $N=30$ (circles), 9 (squares), and 6 (triangles). Reduced time is defined as $t=t^*\sigma(m/\varepsilon)^{1/2}$.

In order to compare results for different chain lengths and in the spirit of scaling laws, we seek the best exponent α which reduces curves for different N to a single one when they are plotted against $t/(N-1)^{\alpha}$. Using the numerical inversion procedure described above, we find consistent values for all properties investigated (see Table II). Figure 4 illustrates this agreement by showing $C_{R^2}(t)$ and $C_{\mathbf{R}}(t)$ vs $t/(N-1)^{1.55}$ for all values of N. Dynamic scaling requires $\alpha = 2\nu + \nu'$ since time should be rescaled by $\tau_N = R_g^2/D_G$. From our last estimate of α, we get $\nu' = 0.38 \pm 0.02$ which lies definitely below the value obtained from $S(k,t)$. We are thus led to conclude that our results do not support a consistent dynamic scaling picture. Whether this inconsistency is a real effect, a consequence of a too-short chain size regime, or an artifact due to boundary effects in simulations remains an open question. Nevertheless all estimates of the dynamic scaling exponent ν' are well below the Rouse prediction $\nu' = 1$, emphasizing once more the role of the solvent in the dynamics of the chain. This is in contrast with the findings of a recent MD simulation on similar systems which suggested a Rouse-type relaxation,[8] to the authors own surprise. We believe that those results cannot lead to any firm conclusion on dynamic scaling, since the length of the simulation runs for the longest chain considered ($N = 20$) was less than 3 times the relevant relaxation time (τ_N).

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[1] D. Ceperley, M. H. Kalos, and J. L. Lebowitz, Phys. Rev. Lett. **41**, 313 (1978); Macromolecules **14**, 1472 (1981).

[2] A. Baumgärtner, J. Chem. Phys. **72**, 871 (1980).

[3] M. van Waveren, M. Bishop, and J. P. J. Michel, J. Chem. Phys. **88**, 1326 (1987).

[4] K. Kremer and K. Binder, Comput. Phys. Rep. **7**, 261 (1988).

[5] M. Bishop, M. H. Kalos, and H. L. Frish, J. Chem. Phys. **70**, 1299 (1979).

[6] D. C. Rapaport, J. Chem. Phys. **71**, 3299 (1979).

[7] W. Bruns and R. Bansal, J. Chem. Phys. **74**, 2064 (1981).

[8] J. Luque, J. Santamaria, and J. J. Freire, J. Chem. Phys. **91**, 584 (1989).

[9] M. Adam and M. Delsanti, Macromolecules **10**, 1229 (1977).

[10] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, New York, 1986).

[11] P.-G. de Gennes, *Scaling Concept in Polymer Physics* (Cornell Univ. Press, Ithaca, 1979).

[12] W. C. Swope, H. C. Andersen, P. H. Berens, and K. R. Wilson, J. Chem. Phys. **76**, 637 (1982).

[13] G. Ciccotti and J. P. Ryckaert, Comput. Phys. Rep. **4**, 345 (1986).

[14] S. Nose, J. Chem. Phys. **81**, 511 (1984); W. G. Hoover, Phys. Rev. A **31**, 1695 (1985), reprinted in *Simulation of Liquids and Solids,* edited by G. Ciccotti, D. Frenkel, and I. R. McDonald (North-Holland, Amsterdam, 1987).

[15] See Ref. 10, p. 106, and references therein.