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Cooperative Relaxations in Condensed Macromolecular Systems. 2. Computer Simulation of Self-Diffusion of Linear Chains

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ABSTRACT: The mechanism of cooperative rearrangements within closed loops of motion is applied for simulation of self-diffusion of linear chains in systems with completely filled space. Center-of-mass displacements, monomer displacements, and autocorrelation functions of the end-to-end vector have been monitored for various chain lengths N up to $N = 512$. Results have shown that the self-diffusion constant is proportional to N^{-1} for short chains and to N^{-2} for longer chains while the motion of monomers for all chain lengths considered is very close to that predicted by the Rouse model. The observed end-to-end vector autocorrelation functions display Williams–Watts-type of behavior with relaxation times and exponents β dependent on the chain length. The nature of topological constraints introduced by the cooperative motion mechanism is discussed.

Introduction

The problem of mobility of long molecular chains in dense systems, the subject of intense study for many years, is still not entirely resolved. The main difficulty consists in correct consideration of topological constraints imposed on chains moving among other chains under the constraint of mutual noncrossability. A number of attempts have been made to treat this problem, for example, by introducing various types of "entanglements"[1-4] or by confining the chain motion to a randomly shaped "tube" formed by obstacles.[5-7]

The progress made in this field to date is extensively reviewed in several papers.[8-10] All these papers indicate, however, a rather unsatisfactory understanding of the dynamics in such systems.

Some efforts have been made to treat the problem by computer simulations.[11-15,31] However, the systems considered have been rather far away from the required condition of dense packing and have usually consisted of relatively short chains.

In the preceding paper of this series[16] the mechanism of cooperative rearrangements was suggested, which involves the diffusive motion of long chains in systems with space completely filled. This mechanism is applied here to computer simulation of self-diffusion of linear chains in dense monodisperse systems. The model used will be called further the "Co–Mo model".

The Model and Computer Simulation Details

The model used in the simulation is the same as that described in the preceding paper.[16] A system of linear chains of freely joined elements on a topologically regular cubic lattice is considered. Each lattice site is occupied so that the chains fill the space completely. The system has periodic boundaries with a linear repeat unit of 32 lattice sites. The repeat volume contains, then, 32^3 lattice sites and the number of unique chains depends on the chain length N as follows:

$$n_N = 32^3/N \tag{1}$$

Equilibrated systems with randomly coiled chains are obtained by the "melting" of regular structures as described in the preceding paper.[16] The main parameters characterizing the equilibrium states of systems with various chain lengths are given in Table I. The chain-length dependence of the mean-squared end-to-end distance $\langle R^2\rangle$ satisfies the relation $\langle R^2\rangle \simeq N^\nu$ with $\nu = 1.015$ and the ratio $\langle R^2\rangle/\langle s^2\rangle$ has a value very close to 6. These two facts indicate that isotropic systems with randomly coiled chains satisfying Gaussian statistics are obtained. Similar results are obtained in other simulations of dense polymer systems performed by different method[26-28] which, however, are not able to generate monodisperse systems.

Table I
Characteristics of Equilibrium States in Systems with Various Chain Lengths[a]

N	n_N	$\langle R^2\rangle$	$\langle s^2\rangle$	$\langle R^2\rangle/\langle s^2\rangle$	$\langle f\rangle \times 10^3$	g
4	8192					
8	4098	10.9	1.84	5.92	0.34	0.77
16	2048	24.6	4.06	6.06	0.04	0.78
32	1024	49.4	8.35	5.92	0.07	0.78
64	512	96.1	16.30	5.90	0.07	0.78
128	256	203.9	33.60	6.07	0.13	0.78
256	128	398.5	68.0	5.86	0.51	0.78
512	64	755.0	126.5	5.97	0.26	0.79

[a] N, chain length; n_N, number of nonidentical chains; $\langle R^2\rangle$, mean-square end-to-end distance; $\langle s^2\rangle$ mean-square radius of gyration; $\langle f\rangle$, orientation factor;[16] g, fraction of "gauche" conformations.[16]

The chains in such equilibrated systems are imagined to move by a cooperative rearrangement mechanism which involves replacements of chain elements along closed loops of motion. An example of a simple rearrangement of this type is shown in Figure 1. Two chains A and B rearrange locally from the state shown in Figure 1a to that in Figure 1c. Monomer segments taking part in the rearrangement are numbered and the way in which they undergo local displacements can be recognized by comparison of their positions in the initial and final states. Additionally, an intermediate state of local configuration (the chain drawn with dotted lines) is schematically illustrated in Figure 1b as a departure from the initial state toward the final state. The directions of related monomer displacements are denoted by arrows which indicate that the displacements form a kind of closed loop of motion. *The* motion takes place within the unshaded area in Figure 1b. The shaded area is effectively not influenced by the rearrangement. Each rearrangement of this type can be regarded as consisting of two types of motion. The first is based on "position exchange" between chain elements belonging to two different chains or belonging to two different parts of the same chain which are in intimate contact. The second type of motion is a translational movement of chain subsegments along the chain contour between subsequent position exchanging areas. The loop of motion shown in Figure 1 contains two position exchange areas (denoted in the figure by dotted rectangles) in which the space occupation by monomer segments belonging to chains A and B changes during the rearrangement. Between these areas the chains are regarded as moving translationally along their contours because the space occupation by el-

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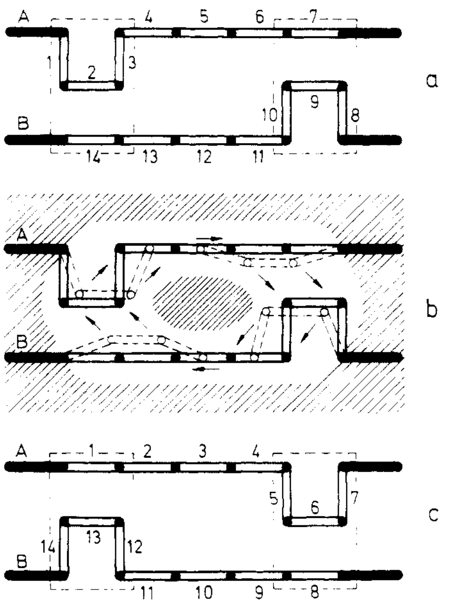

Figure 1. Illustration of a simple cooperative rearrangement in a system completely filled with chains: (a) initial local state; (b) intermediate state (arrows denote directions of element displacements); (c) final state.

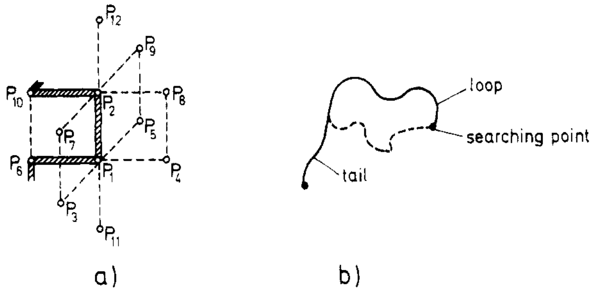

Figure 2. (a) Illustration of the local arrangement of lattice sites taken into consideration when examining the possibilities of "position exchange" (for detailed description see the text). (b) Illustration of the loop searching procedure.

ements of chains A and B is the same before and after rearrangement.

Position exchange occurs only in the neighborhood of special local configurational arrangements of chain subsegments. Situations considered in the current calculations are shown in Figure 2a. To find a possibility for position exchange two adjacent lattice sites P_1 and P_2 on the same chain are analyzed. If the chain element P_1P_2 (between sites P_1 and P_2) forms a kink top (the case shown in the Figure 2a) or if a chain end is found at P_1 or P_2, the neighboring sites are examined in order to find the possibilities for position exchange. This examination includes 10 sites, P_3–P_{12}, shown in Figure 2a. There are 14 situations which have to be considered as potentially allowing the position exchange: the presence of a chain end in one of the sites P_3 to P_{12} (10 possibilities) and four possibilities of finding a chain segment parallel to the segment P_1P_2 (in the case shown in Figure 2a potentially the segments in positions P_3P_7, P_4P_8, and P_5P_9). Examples of various position exchange possibilities are given in ref 16.

Loops of motion are searched according to the following rules: (1) To initialize a motion, an imaginary searching point is positioned at random on an element in the system (monomer unit on a chain). (2) The point is moved in a randomly chosen direction along the chain, searching for a kink top or chain end. (3) If a kink top or chain end is found, the possibilities for position exchange with neighboring chains are examined as described above. (4) One of the accessible possibilities (including the possibility of motion propagation along the same chain) is then chosen at random. (5) When a position exchange is performed the searching point is transferred onto the other chain and the searching procedure according to the above rules is continued, starting again at (2). (6) The loop is closed when the searching point meets his own path. The completed path consists of a loop and a tail as shon in Figure 2b. (7) After the path is completed the structural changes along the tail portion of the path are undone and only the rearrangement within the loop is regarded as a local motion. Each monomer segment within the loop is shifted in this way to adjacent position occupied previously by another element also belonging to the loop.

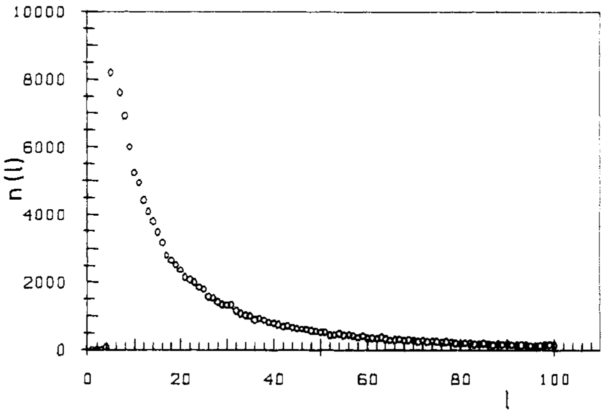

Figure 3. Distribution of lengths of mobile loops in the system of chains with length $N = 512$ (*l* is the number of moved elements in the loop).

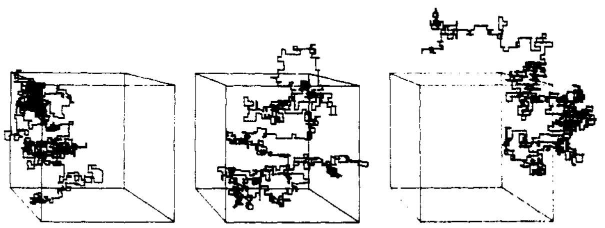

Figure 4. Graphical illustration of computer-simulated chain motion in dense system with chains of length $N = 512$.

The rearrangements performed in the above described way do not influence the identities of individual chains in the system. All chains preserve their lengths and remain unbroken when the system moves.

The above procedure results in a relatively broad loop length distribution. An example of loop length distribution for the system with chain length $N = 512$ is shown in Figure 3. No limits have been imposed on the lengths of mobile loops. Therefore, the motions can be regarded as occurring at very high temperatures.

We have used 10^6 steps of the searching point as a time unit (where the power of 6 is chosen arbitrarily). As will be shown later in Figure 8, such a choice of the time scale results in equal mean-square displacements of the monomer segments being observed within short time intervals in systems with various chain lengths. This means that in the systems studied the frequency of elemental monomer jumps has been assumed to be independent of chain length.

We have noticed that the time scale chosen is proportional to the calculation time. The calculations have been performed on the Honeywell-Bull DPS-8 computer (University of Mainz). The usage of CPU time can be estimated from the time scale in Figure 5, assuming that the unit of time used here is approximately equivalent to 100 CPU seconds.

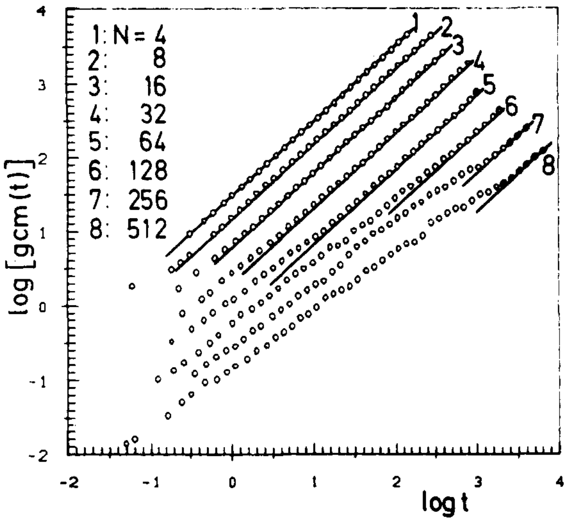

Figure 5. Time dependence of mean-square center-of-mass displacement for the systems with various chain lengths.

The resultant motion of chains is graphically illustrated in Figure 4 by showing contour changes of one chain with time.

Results

To characterize the motion of chains quantitatively, center-of-mass positions $R_{\mathrm{cm}}(t)$ as well as positions $r_i(t)$ of all monomers in the system are monitored. A number of quantities can be determined which describe the dynamics of such systems. We focus our attention on those quantities most frequently reported to facilitate a comparison with theories and with other computer simulation results: (1) mean-square center-of-mass displacement

$$g_{\mathrm{cm}}(t) = \langle [R_{\mathrm{cm}}(t) - R_{\mathrm{cm}}(0)]^2 \rangle \tag{2}$$

(2) mean-square displacement of central monomers

$$g_{\mathrm{c}}(t) = \langle [r_i(t) - r_i(0)]^2 \rangle \quad \text{for} \quad i = N/2 \tag{3}$$

(3) mean-square displacement of chain ends

$$g_{\mathrm{e}}(t) = \langle [r_i(t) - r_i(0)]^2 \rangle \quad \text{for} \quad i = 1 \text{ and } i = N \tag{4}$$

(4) mean-square displacement of central monomers in center-of-mass coordinates

$$g_r(t) = \langle [r_i(t) - R_{\mathrm{cm}}(t) - r_i(0) + R_{\mathrm{cm}}(0)]^2 \rangle \quad \text{for} \quad i = N/2 \tag{5}$$

and (5) end-to-end vector autocorrelation function defined as

$$\rho(t) = \langle R(t)R(0) \rangle / \langle R^2 \rangle \tag{6}$$

where $\langle R^2 \rangle$ is the mean-square end-to-end distance.

Double-logarithmic plots of g_{cm} vs time are shown in Figure 5 for systems with various chain length. The center-of-mass motion displays in all cases a Fickian-type behavior, with g_{cm} linearly dependent on time for long times. The diffusion constants of the center-of-mass were determined as

$$D_{\mathrm{cm}} = \lim_{t\to\infty} [g_{\mathrm{cm}}(t)/t] \tag{7}$$

The chain length dependence of diffusion constants determined in this way is shown in Figure 6. For short chains the diffusion constant is inversely proportional to the chain length while for longer chains the relation

$$D_{\mathrm{cm}} \sim N^{-2} \tag{8}$$

is reached asymptotically.

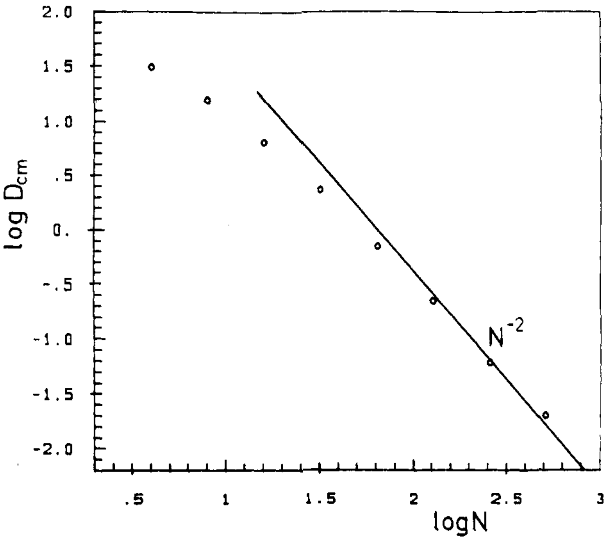

Figure 6. Chain length dependence of the center-of-mass diffusion constant D_{cm}.

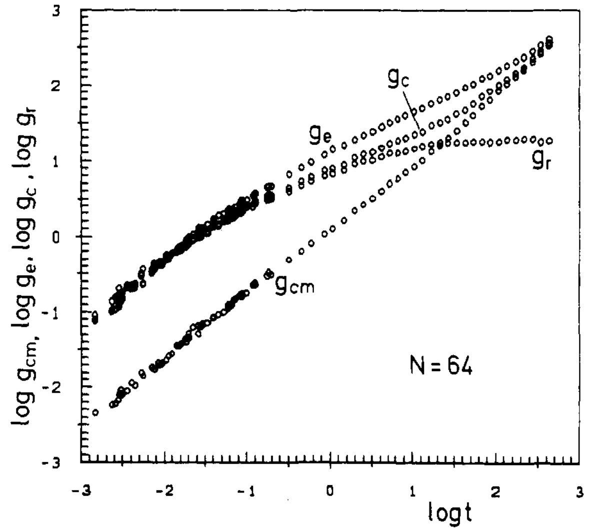

Figure 7. Comparison of time dependencies of monomer displacements with the center-of-mass displacement for the chain length $N = 64$.

A comparison of time dependencies of center-of-mass displacements and displacements characterizing the monomer motion is shown in Figure 7 for the system with chain length $N = 64$. These dependencies are qualitatively the same for all chain lengths. It can be seen that there are three time regimes of different behavior:

(1) At very short times the mean-square displacement of a monomer is proportional to time. In this regime the displacements are the same for chain ends and for central monomers and are independent of the chain length (as shown in Figure 8a).

(2) At very long times the displacements of monomer units coincide with the center-of-mass displacement, hence are proportional to time. In center-of-mass coordinates, the monomer displacement equilibrates in this regime at some plateau, the height of which is dependent on chain length (compare with Figure 8b).

(3) At intermediate times a smooth cross over between the above regimes is observed. Differences are observed between central monomers and chain ends. The latter seem to be slightly more mobile than the former. Exponents characterizing time dependencies of monomer motion in the intermediate regime are determined from slopes of tangents at the points of inflection. They are

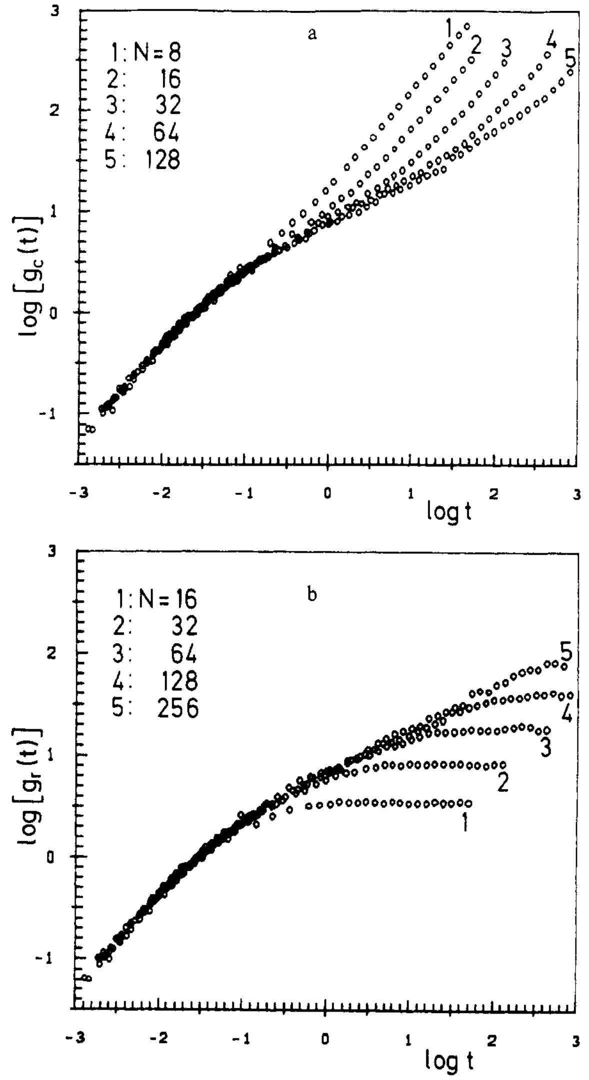

Figure 8. Time dependencies of central monomer displacements for various chain lengths (a) in the laboratory coordinate system and (b) in the center-of-mass coordinate system.

Table II
Parameters Characterizing the Dynamic Behavior of Simulated Systems[a]

N	α_c	α_e	$\log \langle\tau\rangle$	β
8			-0.532	0.92
16			0.034	0.80
32	0.51	0.55	0.786	0.68
64	0.47	0.53	1.580	0.62
128	0.45	0.47	2.374	0.57
256	0.43	0.50	3.403	0.46

[a] α_c and α_e are exponents characterizing time dependences of monomer displacements for central monomers and chain ends, respectively, $\langle\tau\rangle$ is the average relaxation time of the end-to-end vector, and β is the exponent of the Williams–Watts equation.

listed in Table II for central monomers and chain ends separately.

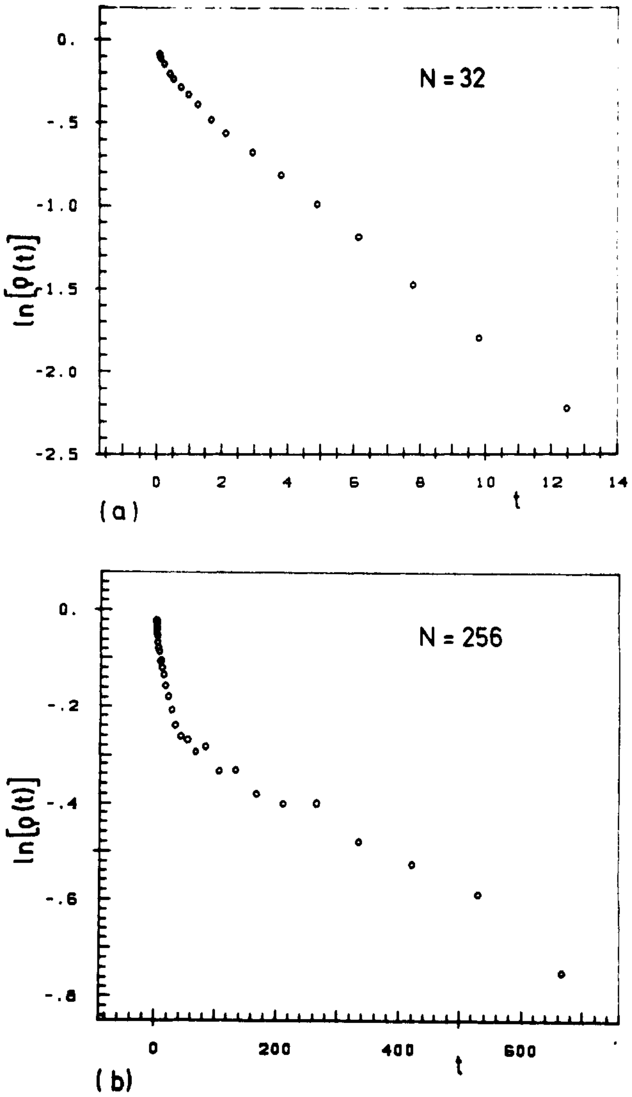

Figure 9. End-to-end vector autocorrelation functions for two chain lengths (a) N = 32 and (b) N = 256.

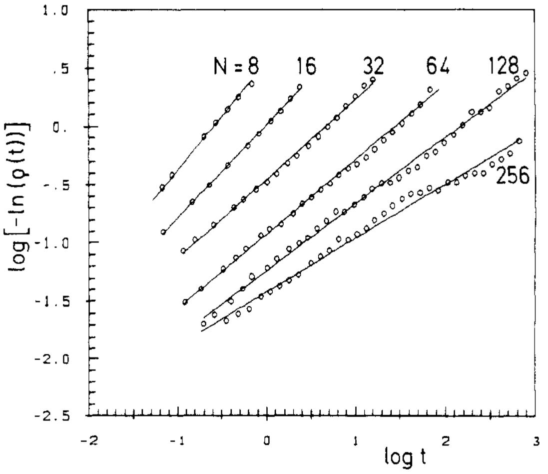

Figure 10. Williams–Watts representation of the end-to-end vector autocorrelation functions for various chain lengths.

Figure 9 shows exemplary end-to-end vector correlation functions for two chain lengths. The decay observed appears to be nearly exponential only at longer times. These long time parts of the correlation functions are used to determine the longest relaxation times. However, the relaxation times so determined appear significantly uncertain especially for systems with longer chains in which the relaxation time values were scattered within a relatively broad range when determined with various choices of time intervals. The uncertainities of the longest relaxation times for systems with various chain lengths are shown in Figure 11.

Another representation of the end-to-end vector autocorrelation functions is shown in Figure 10. It can be seen that these functions follow the stretched exponential form[17]

$$\rho(t) = \rho(0) \exp[-(t/\tau_0)^{\beta}] \qquad (9)$$

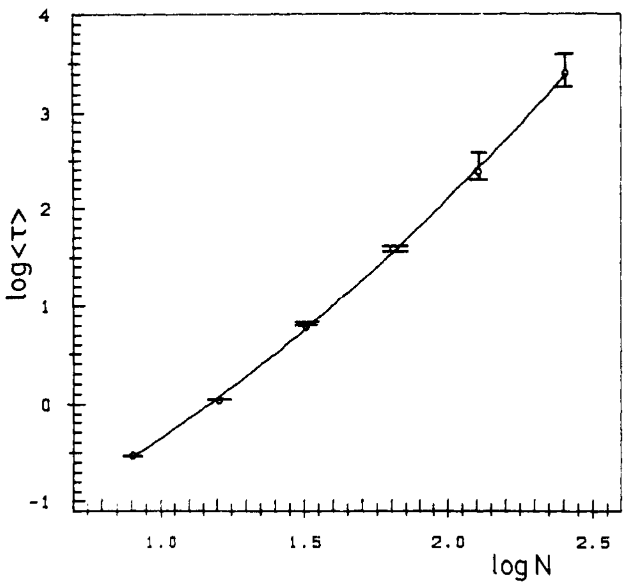

Figure 11. Chain length dependence of the end-to-end vector relaxation times: The bars denote the ranges of values of the longest relaxation times determined from the long time parts of correlation functions. The points denote the mean relaxation times determined by using eq 10.

over the whole time range. Both parameters β and τ_0 appear to depend on chain length. Mean values of the relaxation time $\langle\tau\rangle$ determined according to the formula[18]

$$\langle\tau\rangle = (\tau_0/\beta)\Gamma(1/\beta) \qquad (10)$$

are listed in Table I and ploted in Figure 11 vs chain length. It can be seen that the mean relaxation times determined in this way in systems with short chains are almost the same as the longest relaxation times. In systems with long chains the mean relaxation times are within the range of uncertainity of longest relaxation times. In further considerations we use the mean relaxation times which are determined considering the whole time range and thus are not dependent on the subjective choice of the time range.

Discussion

Existing theoretical predictions concerning the dynamics of linear chains are related to two different models which are supposed to describe chain motions in two extreme cases: (1) in dilute solutions, the Rouse–Zimm model,[19,20] and (2) in bulk polymers, the "reptation" model[6] and its modifications.[7] The models differ in the mechanism of motion assumed. In the first case free motion of an ideal chain is assumed. In the "reptation" model the chain motion is confined into a tubelike region formed by surrounding entangled chains. Our mechanism of motion differs from those assumed in the theoretical models. It is therefore interesting to compare our results with existing theoretical predictions and with other computer simulations.

The molecular weight dependence of the center-of-mass diffusion coefficient is described by the relation

$$D_{\mathrm{cm}} \sim N^{-\alpha} \qquad (11)$$

where the exponent α assumes the value 1.0 for the Rouse model and the value 2.0 for the "reptation" model.

There are very few previous computer simulations which are suitable for comparison with our present results. The results presented here are to our knowledge the first considering self-diffusion of linear chains in truly dense systems, i.e., systems in which all lattice sites are occupied. We can, however, make a comparison with computer simulations of systems with chains at relatively high concentrations but not completely filling the space. Crabb and Kovac[15] obtained $\alpha = 1.69$ for chains on a lattice with a chain length range of 12–48 units and a concentration of 0.9. Baumgartner[14] obtained for the "pearl-necklace" model at concentration 0.7 a molecular weight dependence similar to that obtained in our case (Figure 6) with an exponent asymptotically approaching 2.0 for longer chains.

The latter type of behavior is quite close to experimentally observed dependencies which have shown the validity of $\alpha = 2$ for long chains. This was a source of the initial success of the "reptation" model which, however, as only designed to describe entangled systems of long chains does not attempt to predict the experimentally observed departures from $\alpha = 2$ for short chains.

The theoretical models also predict different behavior for monomers incorporated into the motion of whole chains. According to the Rouse model the mean-square displacement of the central monomer g_{c} should behave differently in three regions of time. At very short times g_{c} should be proportional to t. At intermediate times g_{c} should vary as $t^{1/2}$, and at long times g_{c} should coincide with the mean-square center-of-mass displacement and become again proportional to t. The reptation model predicts that the intermediate regime is split into three regions with the characteristic time dependences $g_{\mathrm{c}} \sim t^{1/2}$, $t^{1/4}$, and $t^{1/2}$.

Several computer simulations have been performed in order to observe the $t^{1/4}$ prediction. Generally the attempts have not been successful[12–15] except for cases where a single chain was only allowed to move among fixed obstacles,[22] for example, by freezing the surrounding chains.[12,13]

In our case only very small deviations from the slope $^1/_2$ in the intermediate region are observed as can be seen in Figure 8, even for relatively high molecular weights. Exact values of the exponents determined for central monomers and chain ends are given in Table II. They show that for long chains such as $N = 256$ the monomer motion is quite different from that predicted by the reptation mechanism but is very close to that expected for the Rouse model. This indicates that the monomers in our model have much more freedom of motion than in the case when restricted only to movements along the chain contour. The same can be concluded from the qualitative observation of chain motions shown in Figure 4.

The above results show that the behavior of systems simulated here is different from predictions of both theoretical models. Such behavior is, however, in two important aspects, compatible with experimental observations related to the dynamics of polymer melts. It was experimentally observed that the molecular weight dependence of the self-diffusion coefficient in polymer melts is proportional to N^{-1} for short chains[25] and to N^{-2} for long chains.[9] On the other hand, neutron scattering experiments[21,30] have shown that the dynamics of local motions in such systems is closer to that predicted by the rouse model although the line shapes of single spectra are to some extent comparable with those predicted for the reptation model.[29]

This shows that the model of motion of chains in condensed systems considered here supplies results which are in good qualitative agreement with both major experimental observations related to center-of-mass motion and monomer motion in polymer melts.

Special attention must be given to the behavior of the end-to-end vector correlation function observed in our systems. Our results show that the chain relaxation in dense systems can hardly be described by the conventional Debye-type relaxation but clearly follows the so-called

Williams–Watts[17] stretched exponential form. The observed coincidence of longest and mean relaxation times can be understood when one considers that for these systems the β values are relatively high. In systems with long chains the clear linear part in the dependence of ln (ρ) vs t was in fact not observed which caused the strong dependence of the longest relaxation times on the choice of the time range.

The stretched exponential type of relaxation behavior is observed in a very wide range of phenomena in materials with strong interactions.[23,24] In our model the interactions are predominantly constraints which restrict motion of any element in the system until some other elements move with this element cooperatively. Taking into consideration a large variety of cooperative rearrangements (various sizes and shapes of loops of motion) as well as a large variety of local structural situations one can expect that the constraints can dominate system relaxations over a very wide range of time scales. This will result in a broad spectrum of relaxation times and consequently lead to the stretched exponential type of relaxation behavior.

The chain length dependence of the average relaxation times (Figure 11) does not follow the relation $\tau \sim N^{\mu}$ with constant μ. The μ values when determined from logarithmic increments of $\langle \tau \rangle$ [$\mu = \Delta(\log \langle \tau \rangle)/\Delta(\log t)$] change from $\mu = 1.88$ for short chains up to $\mu = 3.42$ for longer chains. Calculations for systems with even longer chains are necessary to establish whether a higher values of μ can be observed.

Finally, the essential feature of our model which leads to the observed behavior (in various aspects different from other predictions) will be discussed. In comparison to the Rouse and "reptation" models the main difference lies in the type of topological constraints imposed on chain motion.

As a consequence of the close packing of chains we have introduced the cooperativity of motions which makes the motion in dense system possible. The exact way in which cooperative rearrangements are realized is probably of smaller importance, and some other detailed schemes of cooperative motion can be imagined (for example, kink-jumps in closed loops). In any case, such rearrangements have to involve position exchanges between elements of various chains. This considerably influences the constraints imposed on the chains. The position exchange process provides a mechanism by which a chain can slip among surrounding chains. It is easily imaginable that multiple applications of such processes will involve mutual interslipping of chains in directions lateral to chain contours. In our model the chains cannot move freely as in the Rouse model but they have much more freedom than in the case of reptating chains. Similar behavior of chains has been recently simulated by Kolinski et al.,[31] however, in systems with lower chain concentrations and different mechanism of elemental motions.

We postulate that the space through which a chain can potentially move can be approximated by a system of complicated surfaces. Each such surface includes the whole contour of the considered chain and extends in the system between other chains without crossing them. An almost infinite number of such imaginary surfaces can be drawn for each chain and each surface can extend to infinity. These surface can cross each other constituting an highly complicated imaginary structure which can be regarded as the potential space of chain freedom. The shapes of the surfaces will depend on the sizes of surrounding molecules and will determine the resistance of the medium to the translational motion of the chain. Surface roughness or the degree of surface folding could be introduced as a measure for motion resistance which certainly will depend on molecular weight of the medium and will be higher for long-chain medium than, for example, for solvent medium. These effects will be presented in a subsequent paper where studies of the diffusion of long chains in media with various chain lengths including solvents will be reported.

Conclusions

We have presented results of computer simulation related to the diffusive motion of long-chain molecules in dense systems in which the cooperative rearrangements within closed loops of motion are assumed as the local relaxation mechanism. It was shown that the molecular weight dependence of the self-diffusion constant (center-of-mass motion) coincides for longer chains with the prediction of the reptation model but the time dependence of local motion of monomers is very close to that predicted by the Rouse model.

Such results are obtained due to the weaker topological constraints imposed on chain motion in comparison to the constraints considered for a reptating chain. The cooperativity of motions considered makes any obstacles unstable in time and introduces in this way a broad spectrum of constraint relaxations, which manifests itself in the Williams–Watts type of behavior of the end-to-end vector autocorrelation function.

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