

Chain Motion in an Unentangled Polyethylene Melt: A Critical Test of the Rouse Model by Molecular Dynamics Simulations and Neutron Spin Echo Spectroscopy

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(Received 29 October 1997)

We have investigated the dynamic structure factor for single-chain relaxation in a polyethylene melt by means of molecular dynamics simulations and neutron spin echo spectroscopy. After accounting for a 20% difference in the chain self-diffusion coefficient between simulation and experiment we find a perfect quantitative agreement of the intermediate dynamic structure factor over the whole range of momentum transfer studied. Based on this quantitative agreement one can test the experimental results for deviations from standard Rouse behavior reported so far for only computer simulations of polymer melt dynamics. [S0031-9007(98)05363-0]

PACS numbers: 61.25.Hq

The dynamics of polymer chains in a dense melt could be supposed to pose a theoretical problem requiring a very complex and mathematically involved description. We have to describe a liquid of intertwined threads where each of them has on average excluded volume interactions with \sqrt{N} other threads, where N is the degree of polymerization of the chains. According to all experimental evidence so far, e.g., Refs. [1–3], however, it seems that all these complex topological interactions can be completely neglected as long as the degree of polymerization of the chains is below some critical value, the so-called entanglement molecular weight N_e . For chains longer than N_e the entanglements have to be taken into account [4–7] but for shorter chains the simple Rouse theory [8] is supposed to describe the chain dynamics. Computer simulations of abstract [9,10] as well as atomistic [11] polymer models, on the other hand, show systematic deviations from the Rouse behavior, which can be traced to the interactions between the chains in the melt.

We will show in this paper the first detailed quantitative comparison between a molecular dynamics (MD) simulation of the melt dynamics of an atomistic polymer model and a neutron spin echo (NSE) determination of the single-chain dynamics in the same polymer melt. By establishing the quantitative agreement between simulation and experiment for the internal dynamics of the chains we can then draw conclusions about the validity or shortcomings

of the Rouse model from the combined information of simulation and experiment.

Simulations and experiments were performed on a dense polyethylene melt of n -C₁₀₀H₂₀₂ at 509 K. Experimentally we had already obtained information on the dynamic behavior of longer chain polyethylene (PE) samples at the same temperature from neutron scattering studies [1,2], and we had validated a united atom (UA) model (CH₂ groups treated as one superatom) [12] as well as an explicit atom (EA) model [13] by simulations of shorter chain alkanes. The C₁₀₀ chains are slightly shorter than the entanglement length of PE at this temperature ($N_e = 136$ [2]) and long enough to show Gaussian chain statistics in their conformations [14], thereby making them the ideal test system for a description by the Rouse model. After equilibration for 3 ns we performed a NVT (constant number of particles, volume, and temperature) molecular dynamics simulation of the united atom model (9 ns) as well as the explicit atom model (1 ns) at the experimental density. Details of the models and the simulation technique can be found in [12,13]. For calculating the dynamic structure factor for the UA model we reinsert the hydrogen atoms at positions determined by the neighboring carbon backbone atoms [12].

Our experiments were performed on PE samples which were obtained from a parent (1,4-polybutadiene material)

synthesized by anionic polymerization. PE was produced by subsequent hydrogenation (or deuteration) [15]. The molecular weights of the hydrogenated and deuterated polybutadienes were measured by vapor pressure osmometry yielding 111 C atoms for the protonated and 107 C atoms for the deuterated species, respectively. The molecular weight distribution was obtained from gel permeation chromatography yielding $M_w/M_n = 1.06$. For the NSE experiments a deuterated matrix containing 12% protonated material was used.

The NSE experiments were carried out at the IN11 spectrometer at the Institut Laue Langevin in Grenoble. Two different incoming wavelengths of $\lambda = 6.04 \text{ \AA}$ and $\lambda = 4.35 \text{ \AA}$ were used, in order to cover a dynamic range from 0.08 to 10 ns. The experiments were performed at 509 K studying spectra at seven different momentum transfers ($q = 0.055, 0.1, 0.14, 0.18, 0.22, 0.26$, and 0.30 \AA^{-1}). The experimental background and the background from the deuterated matrix were obtained from separate spin echo scans on a fully deuterated material and subtracted with the proper transmission factors.

In the Rouse model, commonly used to interpret the chain motion in unentangled polymer melts, the chains are treated as Gaussian random coils of monomers connected by entropic springs following a Brownian dynamics (no inertial effects) under the influence of these springs and

an external Gaussian white noise.

$$\zeta d\vec{r}_n(t) = \frac{k_B T}{3\sigma^2} [\vec{r}_{n+1}(t) - 2\vec{r}_n(t) + \vec{r}_{n-1}(t)] dt + d\vec{\eta}_n(t), \quad (1)$$

$$\langle d\eta_{n\alpha}(t) d\eta_{m\beta}(t') \rangle = 2\zeta k_B T dt \delta_{nm} \delta_{\alpha\beta} \delta(t - t'). \quad (2)$$

Here T is the temperature and $\vec{\eta}$ is the Wiener process. The basic length scale is set by the statistical segment length or mean-squared distance between monomers, σ^2 , and the basic frequency is given by the Rouse rate $W = \frac{3\pi^2 k_B T}{\zeta \sigma^2}$, where ζ is the segmental friction coefficient. The model can be solved exactly by Fourier transformation to its normal modes [5],

$$\vec{X}_p(t) = \frac{1}{N} \sum_{n=1}^N \cos\left(p\pi \frac{n}{N}\right). \quad (3)$$

For these modes the model predicts

$$\langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle = \frac{\langle R^2 \rangle}{2\pi^2 p^2} \exp\{-\nu_p t\}, \quad (4)$$

with $\langle R^2 \rangle$ being the mean-square end-to-end distance of the chains and $\nu_p = \frac{p^2}{N^2} W$ being the eigenfrequency of the ν th eigenmode.

Being sums of Gaussian variables the mean-square displacements also are Gaussian distributed, and one can calculate the following result for the single-chain intermediate scattering function in the long chain limit,

$$S(q, t) = \frac{1}{N} \exp\left[-q^2 D_R t\right] \sum_{n,m=1}^N \exp\left[-\frac{q^2 \sigma^2}{6} |n - m|\right] - \frac{2Nq^2 \sigma^2}{3\pi^2} \sum_{p=1}^N \cos\left(\frac{p\pi n}{N}\right) \cos\left(\frac{p\pi m}{N}\right) (1 - e^{-\nu_p t}). \quad (5)$$

Here $D_R = \frac{k_B T}{N\zeta}$ is the center of mass self-diffusion coefficient of the chains. The statistical segment length for PE at 509 K is known experimentally from small angle neutron scattering [16], $\sigma^2 = 13.76 \text{ \AA}^2$, and also for the MD simulation, $\sigma^2 = 15.36 \text{ \AA}^2$ [11], so that the Rouse analysis contains only one free parameter, D_R or W .

This parameter can be furthermore determined independent of any model. For $q \ll \frac{2\pi}{R_e}$, where R_e is the end-to-end vector of the chains, one can observe only the overall diffusion of the chain molecules, $S(q, t)/S(q, 0) = \exp\{-q^2 D_R t\}$. We determined the self-diffusion coefficient for the NSE experiment and the UA simulation from the fit of this diffusive decay to our smallest momentum transfer, $q = 0.055 \text{ \AA}^{-1}$. For the experiment we get a diffusion coefficient of $D_R^{\text{NSE}} = (1.8 \pm 0.15) \times 10^{-6} \text{ cm}^2/\text{s}$ and for the simulation $D_R^{\text{UA}, S(q,t)} = (2.35 \pm 0.03) \times 10^{-6} \text{ cm}^2/\text{s}$. These values can be compared to an extrapolation of pulsed field gradient NMR data for the diffusion coefficient of smaller chain alkanes from Pearson *et al.* [3], which would indicate a value of about $D_R^{\text{NMR}} = 2.3 \times 10^{-6} \text{ cm}^2/\text{s}$ for C_{100} at 509 K. For the MD simulation of the united atom model we also determined the diffusion coefficient directly from the center of mass mean-square displacement of the chains to be $D_R^{\text{UA}, \Delta R^2} = (2.4 \pm 0.3) \times 10^{-6} \text{ cm}^2/\text{s}$ in good agreement with the value from the scattering. Because of the

accumulation of uncertainties involved in the extrapolation in temperature and chain length for the NMR self-diffusion value and also due to some systematic errors for the NSE value (the average chain length in the sample is about $N = 111$, the chains are slowed down compared to the homopolymer case due to the heavier deuterated environment) we regard these values as lying within their mutual error bars.

We can now proceed to determine whether the simulation models really describe the chain relaxation of polyethylene quantitatively by comparing experimental and simulation spectra in scaled time, which is done in Fig. 1. The diffusion coefficient for the explicit atom model (which could not be obtained from the chain center of mass displacements of the 1 ns trajectory) is determined by this data scaling to be $D_R^{\text{EA}} = 1.5 \times 10^{-6} \text{ cm}^2/\text{s}$. In scaled time we see near perfect quantitative agreement between experiment and simulations for all times and momentum transfers. The chain relaxation in the center of mass reference frame therefore is identical between simulation and experiment. This means that conclusions drawn from the mode spectrum and mean-square displacements as observed in the simulations, where the complete atomistic trajectories are available, can be claimed to be also quantitatively valid for the real polymeric material.

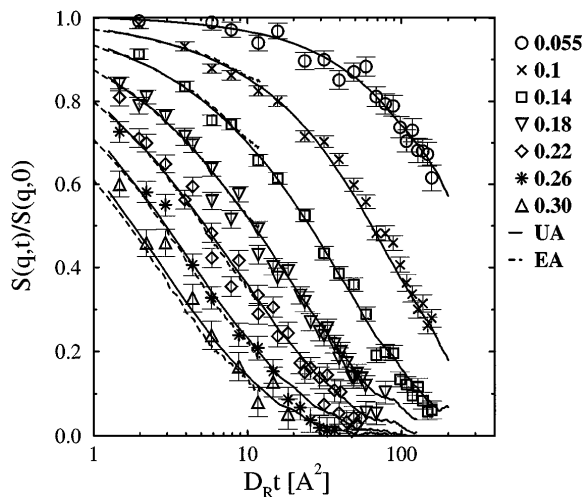


FIG. 1. Dynamic structure factors versus scaled time for experiment (symbols), united atom model (full curves), and explicit atom model (dashed curves). The time axis is scaled by the respective center of mass diffusion coefficients.

The ability of the Rouse model to predict the simulated spectra (all parameters are now known from independent measurements) is tested in Fig. 2. In Fig. 2(a) we show the experimentally determined single-chain intermediate dynamic structure factor for wave vectors ranging from $q = 0.055 \text{ \AA}^{-1}$ to $q = 0.3 \text{ \AA}^{-1}$ and the Rouse prediction. Figure 2(b) shows the same for the simulation. We observe a reasonable agreement of the Rouse prediction with both sets of data for q values up to 0.14 \AA^{-1} , although for times larger than about 4 ns the Rouse curves lie systematically below the observed scattering data. If one tries, on the other hand, to describe the decay for the q values $q = 0.055, 0.1, \text{ and } 0.14 \text{ \AA}^{-1}$ only by the diffusive contribution one obtains good agreement for times larger than 4 ns but severely underestimates the decay on shorter times. For $q \geq 0.18 \text{ \AA}^{-1}$ the theoretical curves lie systematically below both the experimental and simulation data. A combined Rouse fit to the complete experimental spectrum gives the same value for the self-diffusion coefficient of the chains as the fit with the purely diffusive decay to the smallest q value, and consequently the same quality of description of the spectrum. From a mode contribution analysis [1,2] one can show that for the range of momentum transfers studied, the predicted scattering is only sensitive to the modes $p = 0, 1, 2, \text{ and } 3$, i.e., the higher modes contribute only a negligible amount to the decay of the structure factor.

In the simulation we can directly determine the Rouse modes from the trajectory following their definition. We find the following three marked deviations from the Rouse predictions [11]. The center of mass diffusion for times smaller than the Rouse time is not linear but sublinear with an exponent $x = 0.83$. Only the modes $p = 1, 2, \text{ and } 3$ fulfil the dynamic Rouse scaling with $p^2 t$ due to the deviation of the chain structure from Gaussian behavior on smaller scales ($d_p^2 = \langle R^2 \rangle / p$). And finally even these

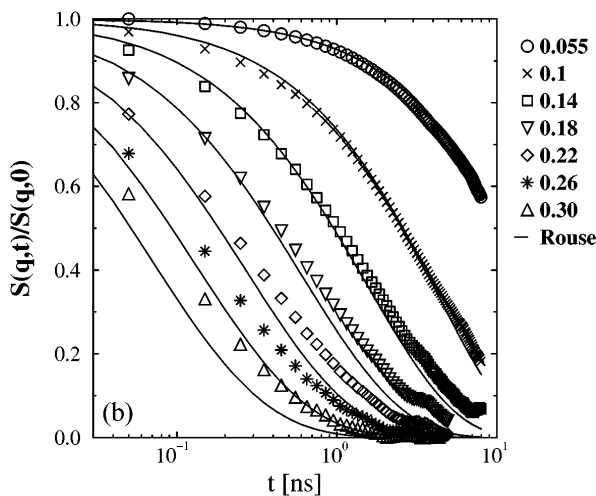
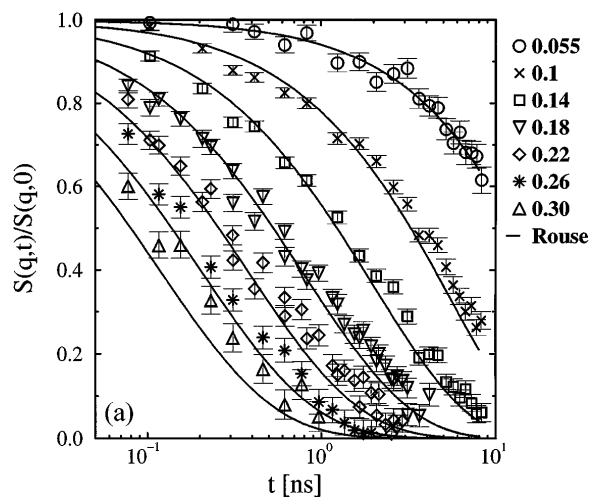


FIG. 2. Dynamic structure factor for $n\text{-C}_{100}\text{H}_{202}$ for the momentum transfers indicated in the legend. The full curves are the Rouse prediction, Eq. (5). (a) Symbols are the neutron spin echo data. (b) Symbols are the simulation data.

modes are not single exponential but show a stretched exponential behavior, $\exp\{-\frac{t}{\tau}^\beta\}$ with $\beta = 0.96$ for the first mode and $\beta = 0.86$ for modes $p = 2, 3$. We have calculated the dynamic structure factor by Eq. (5) but have substituted $D_R t = \frac{1}{6} \langle \Delta R_{\text{cm}}^2(t) \rangle$ and $e^{-\nu_p t} = \langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle / \langle \vec{X}_p^2(0) \rangle$ in order to take explicitly into account the mode behavior obtained from simulation. The agreement in the shape of the curves improved [17], but the quantitative deviations remained.

The only remaining approximation leading to Eq. (5) is the Gaussian assumption $\langle \exp\{-\vec{q} \cdot [\vec{r}_i(t) - \vec{r}_j(0)]\} \rangle = \exp\{-\frac{q^2}{6} \langle [\vec{r}_i(t) - \vec{r}_j(0)]^2 \rangle\}$ for the distribution of the mutual displacements of the monomers at any given time t . This assumption is fulfilled for free diffusion and ballistic and harmonic motion but is in general invalid when more complicated interactions between the moving units are present.

In the Rouse model the Gaussian assumption is exactly fulfilled, but we already saw systematic deviations from the Rouse predictions (like the subdiffusive behavior

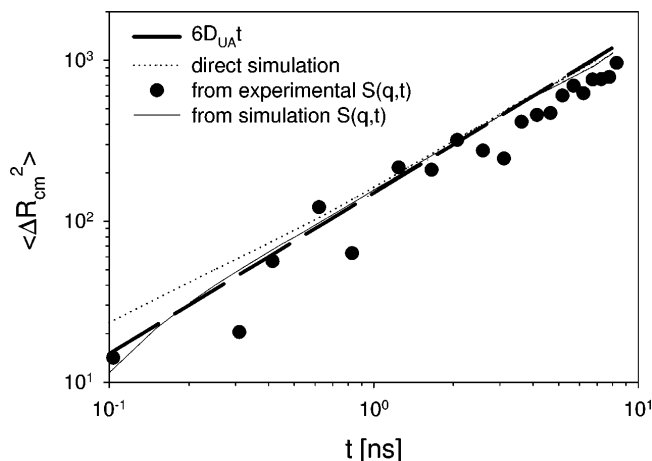


FIG. 3. Mean-square center of mass displacements of the chains as a function of time. Filled circles and the solid line are for experimental and united atom scattering data for $q = 0.055 \text{ \AA}^{-1}$ using the assumption of Gaussian distributed displacements. The dotted line is the mean-square center of mass displacement as determined directly from the simulation trajectories, and the long-dashed curve is the Fickian diffusion behavior with the self-diffusion coefficient determined from the long-time behavior of the mean-square displacement.

of the center of mass of a chain for times smaller than the Rouse time) arising from the interactions between the chains. In Fig. 3 we employ the Gaussian assumption: $S(q, t)/S(q, 0) = \exp\{-\frac{q^2}{6}\langle \Delta R_{cm}^2 \rangle\}$ to infer the mean-square center of mass displacement of the chains from the experimental and simulated structure factors for $q = 0.055 \text{ \AA}^{-1}$. The data are compared to the directly measured mean-square displacement of the chains in the simulation and a Fickian diffusion behavior with the self-diffusion coefficients determined in the simulation. For times larger than the Rouse time (2 ns) we can validate the Gaussian assumption; i.e., the prediction from the scattering and the directly measured mean-square displacement agree, and all curves follow the Fickian diffusion behavior. If we consider times below the Rouse time the differences between the actual displacement, the one predicted by the Gaussian assumption, and the Fickian diffusion curve continuously increase. The actual displacement shows a crossover to a subdiffusive behavior, whereas the scattering data seem to indicate a subdiffusive behavior for times below 1 ns and then a turnover to faster than diffusive behavior for times below 200 ps. The experimental data show much scatter in this time window but seem to be compatible with the trend observed from the dynamic structure factor obtained from simulation.

The overall picture emerging from this combined simulation and experimental effort is that for chains which should be ideal Rouse chains, the model is capable of describing the behavior only on time scales of the order of the Rouse time or larger and therefore on length scales of the order of the radius of gyration of the chains or larger and in the regime where the chains actually show Fickian diffusion. The self-diffusion behavior for times smaller than the Rouse time and the relaxation of the internal modes of the chains show systematic deviations from the Rouse prediction. The interchain interactions also lead to a general failure of the Gaussian assumption in calculating the dynamic structure factor for times smaller than the Rouse time.

G.S. acknowledges support by the SFB262. We would like to thank K. Binder for helpful discussions. A generous grant of computer time at the computer center of the University of Mainz is gratefully acknowledged.

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