Chain confinement and anomalous diffusion in the cross over regime between Rouse and reptation

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ABSTRACT: By neutron spin echo (NSE) and pulsed field gradient (PFG) NMR we study the dynamics of a polyethylene-oxide melt (PEO) with molecular weight in the transition regime between Rouse and reptation dynamics. We analyze the data with a Rouse mode analysis allowing for reduced long wavelength Rouse modes amplitudes. For short times sub-diffusive center-of-mass mean square displacement $\langle r_{com}^2(t)\rangle$ was allowed. This approach captures the NSE data well and provides accurate information on the topological constraints in a chain length regime, where the tube model is inapplicable. As predicted by reptation for the polymer $\langle r_{com}^2(t)\rangle$, we experimentally found the sub-diffusive regime with an exponent close to $\mu = \frac{1}{2}$, which, however, crosses over to Fickian diffusion not at the Rouse time, but at a later time, when the $\langle r_{com}^2(t)\rangle$ has covered a distance related to the tube diameter.

Dynamics of polymer melts is multiscale, extending from the local monomer motion to diffusion over the distances beyond the size of the whole chain.[1–3] As an elementary constituent of the polymer chain a coarse-grained segment consisting typically of several main chain bonds is considered. In the context of inter segmental interactions, two approaches are used. The Rouse model based on the Langevin equation of segmental motion accounts for entropic forces within a chain, stochastic forces and friction with the surrounding media.[4,5] Interactions between the segments of the other chains are not considered. In the reptation model, the inter-chain interactions lead to the confinement of the polymer chain in a tube built by the neighboring chains.[1,6] It was shown that for relatively short chains ($M<M_c$, M_e) with M_c critical molecular weight and M_e entanglement molecular weight, where the inter-chain interactions are not pronounced, the Rouse model provides a good description with physically realistic parameters of the chain dynamics.[5] Dynamics of long or strongly entangled chains can be successfully described by the reptation model. Whereas, the intermediate range of polymer chain lengths is less understood.

In the mode coupling theory (MCT) approach of Schweizer and coworkers,[7–10] the tube ideas are replaced by strong nonlinear couplings between collective density fluctuations on the scale of the chain radius of gyration R_g. MCT leads to slowly fluctuating intermolecular forces that overcome the fast local dynamics rapidly.[5] The model predicts many aspects of polymer melt dynamics, but due to approximations does not contain anisotropic motion that by assumption is part of the tube model. Guenza considered a generalized Langevin equation (GLE),[11] where, as a result of chain interpenetration, the chain motion is coupled within the range of its R_g by a Gaussian interchain potential of mean force.

As shown recently, short tracer chains in a highly entangled polymer matrix move cooperatively demonstrating sub-diffusive behavior over a distance on the order of the reptation tube diameter.[12] Beyond this cross-over distance, the Fickian diffusivity agrees with the macroscopic results. In addition, we found that the Rouse dynamics of the tracers is non-Gaussian with a related segment displacement distribution narrower than the Gaussian counterpart. This is a consequence of highly cooperative motion of the tracers with the host that mirrors the host dynamics within the tube. This finding contradicts the common reptation theory that within the tube constraints considers decoupled Rouse motion in the heat bath provided by the surrounding chains. The phenomena were generically found both in a polyolefin (polyethylene) as well as in a polyether (polyethylene-oxide).[12,13]

The cooperative motion of polymer chains in the regime of entanglement formation overlaps and/or competes with the increasing tube confinement of the chain complicating the experiments and theoretical investigations. In the intermediate regime the concept of reptation tube is not fully applicable because the tube itself is not yet fully developed whereas, the confinement effects from the neighboring chains become more important.

Extensive MD simulations on the chain dynamics by Kremer et al. demonstrated that the Rouse and reptation models work quite well in the limit of short and long chain dynamics respectively.[14] Kalathi et al. performed coarse-grained simulations using the Kremer and Grest model for chain lengths, where entanglement effects become prominent and found that the Rouse modes of weakly entangled chains show characteristic trends in the relevant parameters, such as an assumed mode stretching and characteristic relaxation rates.[15] Halverson et al.[16] using MD simulations demonstrated that with increasing chain length, the polymer center-of-mass diffusion becomes increasingly sub-diffusive on a time scale shorter than the Rouse time τ_R.

Here, we report combined NSE and PFG-NMR investigation on weakly entangled poly(ethylene oxide) (PEO) in a broad temperature interval on time scales from hundred picoseconds to hundreds of nanoseconds reflecting the transition regime from Rouse to reptation behavior. We show that the dynamics of weakly entangled chains is well understood in terms of a Rouse mode analysis that delivers the confinements imposed by the emerging entanglement network. As predicted by reptation for the polymer center-of-mass mean square displacement $\langle r_{com}^2(t)\rangle$ we found the sub-diffusive regime with an exponent close to $\mu = \frac{1}{2}$, which, however, crosses over to Fickian diffusion not at the Rouse time, but at a later time, at which the $\langle r_{com}^2(t)\rangle$ has covered a distance related to the emerging tube diameter. To the best of our knowledge, this is the first experimental observation of this sub-diffusive regime.

NSE experiments were performed at the spectrometer IN15 at the Institut Laue-Langevin (ILL).[17] Employing a neutron wavelength of λ=14 Å we studied a blend of h-PEO (10%, M_w=8130 g/mol, M_w/M_n=1.01, number of segments/chain N=185) with d-PEO (90%, M_w=8252 g/mol, M_w/M_n=1.01, N=172) at different temperatures from 350 K to 450 K covering the time range 0.1<t<550 ns at momentum transfers, Q=0.05, 0.078, 0.096, 0.13 and 0.15 Å^{-1}. Details of the polymer synthesis are given in supporting information (SI).

Long range Fickian diffusion coefficients, D_{Fick} were determined using Pulse Field Gradient – Nuclear Magnetic Resonance (PFG-NMR) in temperature range 338K to 450K with a magnetic resonance analyser Bruker Minispec (mq20) operating at ^{1}H frequency of 20 MHz and equipped with a permanent magnet. The attenuation of the echo signal from a pulse sequence containing a magnetic field gradient pulse is used to measure the translational diffusion of the molecules (hydrogens) in the sample at the time scale of tens of milliseconds. During this time the protons are able to overcome the distances of order of hundreds of nanometers. D_{Fick} reported in Table 1 were measured using a standard stimulated echo (STE) pulsed-field-gradient sequence.

Table 1. Temperature dependent Fickian diffusion coefficients for center of mass polymer diffusion in the PEO8K melt as measured by PFG-NMR.

T / K	338	343	350	375	400	415	430	450
D_{Fick} x 10^{-12} m^2 s^{-1}	0.49	0.57	0.98	1.20	2.24	2.64	3.42	4.21

Figure. 1 displays the Arrhenius representation of diffusion data with an activation energy E_a = 22.0±1.0 kJ/mol or 228±10 meV.

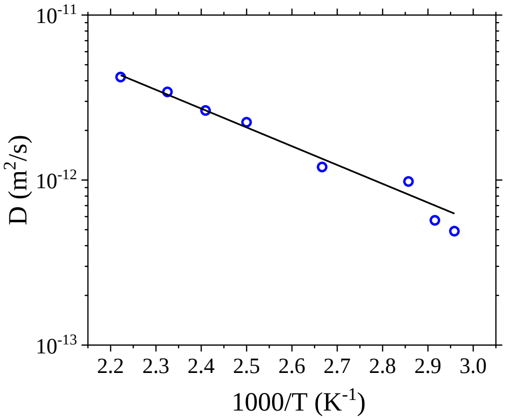

Figure 1. Fickian diffusion coefficients measured for the PEO melt as obtained from PFG-NMR, presented in an Arrhenius plot.

Figure 2 presents the NSE spectra obtained at 4 different temperatures. Within the time window of IN15 at higher Q the spectra fully decay, thus, excellently covering the dynamic features of the PEO melt on the molecular scale.

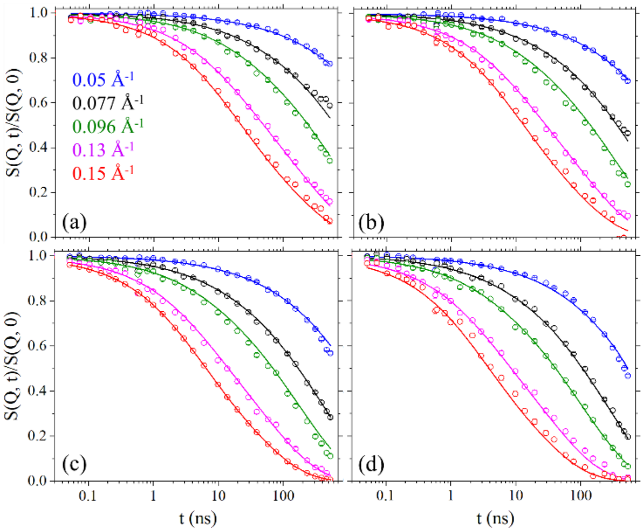

Figure 2. NSE spectra from the PEO obtained at different temperatures: (a) 350K, (b) 375K, (c) 415K and (d) 450K at various Q values as indicated. The lines show the results from the joint fit of all spectra at all temperatures (see text).

PEO exhibits M_e~1.6 - 2.0 kg/mol.[18,19] Our sample (M_w=8 kg/mol) is subject to about four entanglements thus, representing the weakly entangled regime. To account for the effect of the emerging chain confinement, the NSE data were evaluated in terms of a Rouse mode analysis, where we varied the amplitudes of different contributing Rouse modes.[20,21] This analysis allows to scrutinize the spatial confinement of the chain motion in assigning smaller amplitudes to the low indexed Rouse modes. However, not altering τ_p, the analysis does not properly describe τ_p associated with the topological confinement. In the discussion section we demonstrate that in order to evaluate the apparent chain confinement, the Rouse mode analysis is a valid approach and is nearly independent from the physically necessary modifications of τ_p. We describe the magnitude of the changing Rouse mode amplitudes from low to high mode numbers p by a Fermi function:

$$f_{trans}(p) = \frac{1}{1 + exp\left(\frac{p_{cross} - p}{p_{width}}\right)} \tag{1}$$

The choice of such a function ensures systematic fitting results by preventing arbitrary and unphysical changes in Rouse mode amplitudes. Fit parameters in Eq. (1) are p_{cross} and p_{width}. Including Eq. (1), the single chain Rouse dynamic structure factor assumes the form:

$$S(Q,t) = \frac{1}{N} exp\left(-\frac{1}{6}\langle r_{com}^2(t)\rangle Q^2\right) \sum_{n,m}^{N} exp\left\{-\frac{1}{6}Q^2|n - m|l_{seg}^2\right\} exp\left\{-\frac{2}{3\pi^2} R_e^2 Q^2 \sum_p^N \frac{1}{p^2} f_{trans}(p) cos\left(\frac{p\pi n}{N}\right) cos\left(\frac{p\pi m}{N}\right)\left(1 - exp\left[-2w\left(1 - \cos\left(\frac{p\pi}{N}\right)\right)t\right]\right)\right\} \tag{2}$$

With N: number of monomers; $\langle r_{com}^2(t)\rangle$: center of mass displacement; $R_e^2 = l_{seg}^2 N$: chain end to end distance; l_{seg}: monomer length; $w = \frac{Wl^4}{l_{seg}^4}$: elementary relaxation rate and the scale independent "Rouse rate" $Wl^4 = \frac{3k_B T l_{seg}^2}{\xi_0}$; with k_B the Boltzmann constant; T the absolute temperature and ξ_0 the monomeric friction coefficient.

Recently it was shown that unentangled chains in the Rouse regime exhibit a transition from sub-diffusive center of mass displacements $\langle r_{com}^2(t)\rangle$ to Fickian diffusion around their Rouse time[22], whereas for tracer diffusion in highly entangled melts this transition occurs, when their $\langle r_{com}^2(t)\rangle$ reaches the size of the tube diameter. With this in consideration, and following the prediction of reptation, we allow the $\langle r_{com}^2(t)\rangle$ to exhibit a cross over from sub-diffusion at short times to Fickian diffusion at longer times fitting the cross over displacement $\langle r_0^2\rangle$.

$$\langle r_{com}^2(t)\rangle = \left(\left(e^{-log(\langle r_0^2\rangle/(6D_{Fick}))\mu}\,\langle r_0^2\rangle\, t^{\mu}\right)^{a_{cross}} + (6\,D_{Fick}\,t)^{a_{cross}}\right)^{1/a_{cross}} \qquad (3)$$

With μ the time exponent for sub-diffusion and a_{cross} an exponent describing the sharpness of the cross over; we took a_{cross}=8. We note that by allowing $<r^2_{com}(t)>$ to be sub-diffusive at shorter times, we do not rule out the possibility that some of the lower p Rouse modes might be stretched as has been shown in literature,[23,24] where stretching parameters such as $\beta = 0.86..0.96$ were reported. We tried to vary β by taking an initial guess at β = 0.8, which does not change the quality of our fit, neither does it change the value of β, if fitted. In order to minimize the fitting parameters, we did not invoke further mode sub-diffusivity.

We jointly fitted NSE data for all Q values at all temperatures by fixing D_{Fick} to the PFG-NMR values. $\langle r_0^2\rangle$, μ and the parameters defining $f_{trans}(p)$ were used as global parameters for all the data sets. The temperature dependence of Wl^4 was varied using activation energy obtained from the PFG-NMR by fitting the joint prefactor only. As shown in Figure 2, excellent fits for all the NSE spectra are achieved.

The joint fit results in the global parameters for f_{trans}: $p_{cross} = 4.23 \pm 0.12$, $p_{width} = 0.61 \pm 0.086$. For the sub-diffusivity, we observe very interesting features: For all temperatures sub-diffusivity is well described by a common μ=0.53±0.002. Furthermore, the cross-over to Fickian diffusion is observed to take place after the center of mass has covered an $\langle r_0^2\rangle$=1782±16 Å^2 or a distance 42 Å, a value in the order of the tube diameter d for PEO - from rheology d=34.5 Å,[25] while microscopic observation by NSE delivered d=48 Å.[26]The exponent μ is very close to the prediction of reptation (μ=1/2), which to the best of our knowledge is the first experimental validation of this prediction. However, we observe a crossover to Fickian diffusion, when the center of mass displacement has reached the size of the emerging tube. In contrast, common tube theories predict a $\langle r_{com}^2(t)\rangle \sim t^{1/2}$ until it crosses over to Fickian diffusion around $\tau_R{}^2$.[6,16] This finding is in line with earlier observations of short tracer diffusion in highly entangled hosts, where the cross-over of the center of mass diffusion to Fickian diffusion was also observed at the time, when $\langle r_0^2\rangle$ has reached the size of the tube.[12,13] There, we hypothesized that the cooperativity of chain motion is responsible for the expansion of the sub-diffusive region to a time scale that corresponds to the tube diameter, beyond which Fickian diffusion is observed. We note that a common cross-over $\langle r_{com}^2(t)\rangle$ is not artificially produced by the fit. Fitting $\langle r_0^2\rangle$ separately for each temperature does not change $\langle r_0^2\rangle$ significantly as shown in Table 2.

Table 2. Fitting parameters obtained for the PEO using Eqs.(1)-(3).

T / K	D_{Fick} (m^{2}s^{-1})*	$Wl4$ § / Å^{4}ns^{-1}	μ $^{\#}$	$\langle r_0^2\rangle$ † / Å^2 $^{\&}$
350	0.75x10^{-12}	5810	0.529	1782 (1846±23)
375	1.29x10^{-12}	9698	0.529	1782 (1986±24)
415	2.66x10^{-12}	19106	0.529	1782 (2032±21)
450	4.51x10^{-12}	31476	0.529	1782 (1797±17)

*fixed from PFG-NMR; §error bar for joint fit ± 370 Å^{4}ns^{-1}; #error bar for joint fit ± 0.001; † error bar for joint fit ± 16 Å^2; & the values in brackets display the results for $\langle r_0^2\rangle$ from separate fits. The apparent discrepancy between the individual fit results and the that of the joint fit shows that beyond the quoted statistical errors parameter correlations in the fitting procedure also may influence the outcome. Within all these constraints the proper error margin might be in the order of ±100 – 200 Å^2.

The obtained f_{trans} (Eq. (1)) is displayed in Figure 3. Systematically suppressing the long wavelength modes, f_{trans} efficiently captures the topological constraints imposed by entanglements. The inflection point of p_{cross}=4.3 remarkably agrees with the entanglement number of about 4 corresponding to M_w=8 kg/mol of our PEO. Therefore, although chosen phenomenologically, the fitted Fermi function is able to quantitatively capture the constraints to the conformational dynamics of chain portions with $M_w > M_e$ which renders the unobstructed relaxation of these modes unfeasible. It is noteworthy that any other transition function capable of systematically suppressing the lower Rouse modes should be able to capture these features.

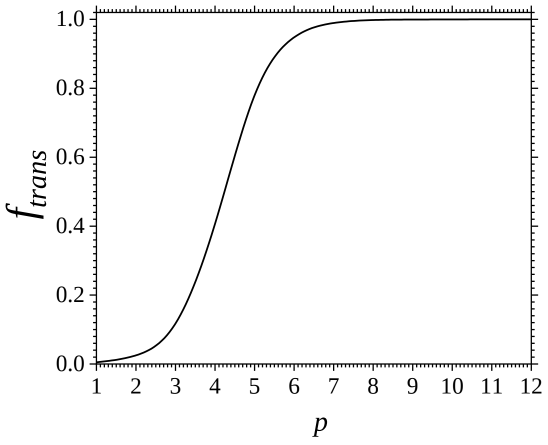

Figure 3. Transition function governing the mode-amplitudes in the Rouse analysis f_{trans} for the PEO melt.

Taking n=m in the limit t→∞, Eq. 2 provides information about the limiting or asymptotic internal mean square displacement (MSD) of each segment along the chain (relative to the center of mass).

$$\langle r_n^2(t \to \infty)\rangle = \frac{4}{\pi^2} R_e^2 \sum\nolimits_{p=1}^{N} \frac{1}{p^2} f_{trans}(p)\, cos\left(\frac{p\pi n}{N}\right)^2 \qquad (4)$$

Figure 4 presents the thus calculated asymptotic MSD for the monomers along the chain as a function of the monomer number (n).

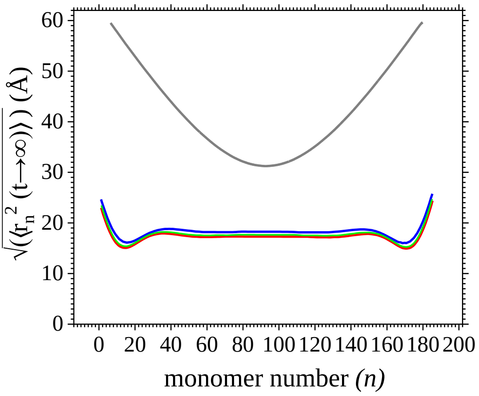

Figure 4. Square root of the asymptotic internal monomeric MSD for a polymer chain in the PEO melt as a function of monomer number along the chain (red line); the blue and green lines mark the corresponding MSD under the assumption of a modified relaxation time dispersion (see text). Grey line shows the monomeric MSD of a Rouse chain calculated without reduced mode amplitude.

Qualitatively $\sqrt{\langle r_n^2(t\rightarrow\infty)\rangle}$ displays the expected behavior: In the interior of a chain in the melt, the entanglement related chain confinement is clearly visible. Towards both chain ends the limiting MSD grows indicating the absence of constraints at the ends. The weak oscillations relate to the Fourier type description of the segmental motion, where finite size effects occur. The average displacement size is about 17-18 Å, which corresponds to approximately half of the tube diameter. This is a remarkable result, which is obtained without invoking more involved detailed analysis such as the anisotropic motion of polymer chain, as postulated by the pristine tube model. Note that in our reported Fourier time range, the dynamic structure factor (Figure 2) does not yet display any plateau, which in the absence of a detailed theory makes it impossible to obtain the tube effects directly from the data. However, the Rouse mode analysis approach directly captures the transient topological confinements of the chain due to the emerging tube constraints, which otherwise requires a valid theory describing the chain dynamics in the cross over region from Rouse to reptation dynamics. The dynamics of a Rouse chain without mode restrictions presented in Figure 4 for comparison does not show any plateau but a gradual increase of the limiting displacement from central to the end monomers. We note that our approach has some analogy to the switching function approach reported by Schweizer and Szamel in context of the MCT.[10]

As it is well known, for a polymer melt in the cross over regime from Rouse to reptation dynamics not only confinement is established but also the spectrum of the relaxation time is changing.[20,21] We show in the SI that such changes in relaxation time spectrum only marginally affect the results of confinement (Figure S1 and S2).[27] We rationalize this by considering an extreme case of a Fermi-step function. Then any relaxation change following this function (i.e. retardation of lower modes) would not be noticeable if the same step function is used to zero the amplitudes i.e. the retardation of the lower mode amplitudes would make the variation of the relaxation spectra infinitely free. For a somewhat smoother transition, this will still hold up to some degree. In combination with the approximate interchangeability of rate and amplitude modulation within the finite time-Q range of NSE, the above observation is not too surprising.

We conclude that the confinement largely bases on the modification of the mode amplitudes obtained from a Rouse mode analysis. Changing τ_p in addition, only very weakly affects the confinement. Finally, we note that by varying the relaxation spectrum without imposing confinement (retardation of the Rouse modes) the NSE data cannot be fitted.

We summarize the key results from Rouse mode analysis of weakly entangled PEO melt as follows:

- We achieved an excellent data description in terms of the applied model covering all twenty spectra at 4 different temperatures using a joint fit with common parameters.
- For the center of mass displacement, we experimentally established the predicted $t^{1/2}$ regime.
- However, consistent with previous observations on short tracer chains in a highly entangled polymer matrix,[12,13] the cross-over to Fickian diffusion takes place not at the Rouse time, but at a later time, when the center-of-mass $\langle r_{com}^2(t)\rangle$has covered a distance corresponding to the tube diameter.
- The Rouse mode analysis led to the reduction of low mode number amplitudes reflecting the emerging confinement that for higher molecular weights would represent the tube.
- The resulting limiting monomeric MSD in the center of mass system of the chain reflects the emerging chain confinement.

ASSOCIATED CONTENT

Supporting Information:

(1) Synthesis details for the hydrogenated and deuterated polyethylene oxide; (2) NSE data analysis using cross-over functions for p-dependence of the mode relaxation times and Rouse mode amplitudes; (3) Relaxation spectra calculated for different model parameters.

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Author Contributions

All authors have given approval to the final version of the manuscript.

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Table of Contents artwork

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