The confined-to-bulk dynamics transition of polymer melts in nanoscopic pores of solid matrices with varying pore diameter

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Abstract. The confinement of polymer melts in nanoscopic pores leads to chain dynamics significantly different from bulk behaviour. This so-called ‘corset effect’ occurs both above and below the critical molecular mass and induces dynamic features as predicted for reptation. The confined-to-bulk dynamics crossover is treated analytically on the basis of general thermodynamic relations connected to the fluctuation of the number of particles (Kuhn segments) in a given volume. Bulk behaviour is shown to occur only if the pore diameter complies with the limit $d_{pore} \gg (b^3/k_BT\kappa_T)^{1/3}RF \approx 10R_F$, where $b$ is the Kuhn segment length, $\kappa_T$ the isothermal compressibility, $T$ the temperature, $k_B$ the Boltzmann constant and $R_F$ the Flory radius. For smaller pores, the confined polymer chains reptate along their own contours in tubes with an effective diameter $d \approx \sqrt{b^2\rho_s k_BT\kappa_T} \approx 0.5 \text{ nm}$, where $\rho_s$ is the number density of Kuhn segments. From the theoretical point of view, the crucial factors on which the corset effect is based are (i) impenetrable pore walls, (ii) low compressibility and (iii) the uncrossability of polymer chains.
1. Introduction

We have previously demonstrated that chain dynamics in melts of linear polymers confined in nanoscopic pores of solid matrices consisting of strongly cross-linked polymers is significantly different from that in melts in bulk [1]–[4]. These studies were carried out using field-gradient NMR diffusometry [5] and proton or deuterium field-cycling NMR relaxometry [6]. Linear polyethylene oxide was studied in bulk and confined in a porous methacrylate matrix (see figure 1). Different samples with mean pore diameters ranging from approximately 8–58 nm were prepared and examined [7, 8]. The experiments were performed with polyethylene oxide of different molecular masses both below and above the critical value, \( M_c \), which indicates the crossover between the so-called unentangled and entangled chain dynamics [9, 10].

In the following, we will focus on the frequency dependence of the spin-lattice relaxation time \( T_1 \) as an indicator of the type of polymer-chain dynamics in the frequency range from less than a kHz up to several hundred MHz. We will first briefly review the diverse formalisms and model predictions for the spin-lattice relaxation dispersion of polymers together with experimental facts, and then discuss the difference between bulk and confined chain dynamics. The main objective of this paper is to elucidate under which conditions the transition from bulk to confined dynamics occurs. A corresponding estimation will be presented.

2. Theoretical and experimental background

2.1. Rouse dynamics for bulk polymer melts with \( M_w < M_c \)

Chain dynamics in bulk polymer melts with molecular masses \( M_w < M_c \) can be described very well on the basis of the Rouse model [11, 12]. The consequence for the frequency dependence of the spin-lattice relaxation rate is the prediction [3], [13]–[16]

\[
\frac{1}{T_1^R} = 0.63 \tilde{M}_2 \tau_s \ln \left( \frac{0.95}{\omega \tau_s} \right) + 0.63 \tilde{M}_2 \tau_s = C_1 \tau_s \ln \left( \frac{1}{\omega \tau_s} \right) + C_2 \tau_s. \tag{2.1}
\]
Figure 1. Typical freeze-fracture electron micrographs of semi-interpenetrating networks formed of cross-linked methacrylate and linear PEO ($M_w = 6000$). The ‘worm-like’ structures represent PEO that was contained in pores with a diameter of about 10 nm.

The coefficients in equation (2.1) have been obtained by direct numerical evaluation of the normal-mode solutions of the Rouse equation of motion and are somewhat modified relative to those given in [14]–[16]. This relatively weak frequency dependence was verified in numerous experiments [13]. The second term on the right-hand side is the low-frequency contribution of all local fluctuations within the Kuhn segments, which are usually called component A fluctuating with a time constant $\tau_s$. The quantity $\tilde{M}_2$ is the residual second moment of spin interactions after averaging over all fast fluctuations occurring on a time scale $t \ll \tau_s$. The quantity $\tilde{M}_2^*$ represents the second moment, characterizing the initial value of the correlation function for component A. The parameters to be fitted to experimental data are $C_1$, $C_2$ and $\tau_s$. Equation (2.1) is valid for polymers with molecular masses $M_w < M_c$ and for frequencies in the range $\tau_R^{-1} < \omega < \tau_s^{-1}$, where the ‘Rouse relaxation time’ is given by $\tau_R = N^2 \tau_s$, with $N \propto M_w$ the number of Kuhn segments per chain. At lower frequencies, $\omega \ll \tau_R^{-1}$, the spin-lattice relaxation time can be described by

$$\frac{1}{T_R^1} = 0.7 \tilde{M}_2 \tau_s \ln(0.35 N^2) + 0.7 \tilde{M}_2^* \tau_s = C_1^* \tau_s \ln(M_w^2) + C_2^* \tau_s,$$

(2.2)

where $C_1^*$, $C_2^*$ and $\tau_s$ are fitting parameters.

2.2. Renormalized Rouse dynamics for bulk polymer melts with $M_w > M_c$

The proton $T_1$ frequency dependence of bulk polymer melts above the critical molecular mass is characterized by different power-law regions predicted by the renormalized Rouse theory [13, 17], which is based on the Schweizer original ansatz [18]

region I: $T_1 \propto M_w^0 \omega^{1/2}$,

region II: $T_1 \propto M_w^0 \omega^{1/3}$...

region III: $T_1 \propto M_w^0 \omega^{2/3}$...

(2.3)
The ranges in the exponents cover the predictions for different renormalization orders [13]. Regions I and II correspond to the ‘high-’ and ‘low-mode number limits’, respectively, as defined in [13, 17]. High chain mode numbers, \( p > N/6\pi \), are relevant on a short time scale, i.e. in the limit of high frequencies. At lower frequencies, the ‘low-mode number limit’ applies for \( p < N/6\pi \). It is difficult to specify in absolute terms what ‘high’ or ‘low’ frequency means, since this is a matter of the polymer species and the temperature. In particular, varying the temperature shifts the crossover between regions I and II. A corresponding discussion and many experimental examples can be found in [13].

Region III is finally expected at even lower frequencies when inter-segment dipolar interactions start to dominate the spin-lattice relaxation mechanism [19]. The inter-segment character of this phenomenon excludes any relevance for quadrupole nuclei such as deuterons, where relaxation is dominated by intra-segment spin interactions. Actually the nature of the region III process can be experimentally identified unambiguously in this way.

2.3. Reptation dynamics for polymers confined in tubes

In his pioneering 1971 paper [20], de Gennes predicted limiting laws for the spin-lattice relaxation dispersion of a polymer chain ‘reptating’ about fixed obstacles. Polymer motions are supposed to be constrained by an impermeable, rigid tube. The tube/reptation model was later elaborated in more detail by Doi and Edwards [10], who defined four dynamic limits on the basis of which the spin-lattice relaxation dispersion can be predicted. See [13] for a complete discussion. Of particular interest in the present context are

\[
\text{limit (II)}_{DE} \quad \text{for } 1/\tau_R < \omega < 1/\tau_e, \quad T_1 \propto M_w^{0}\omega^{3/4}, \tag{2.4}
\]

\[
\text{limit (III)}_{DE} \quad \text{for } 1/\tau_d < \omega < 1/\tau_R, \quad T_1 \propto M_w^{-1/2}\omega^{1/2},
\]

where \( \tau_e \) is the so-called ‘entanglement time’, i.e. the mean time a segment needs to experience the tube constraint first, and \( \tau_d \) is the ‘tube disengagement time’ specifying how long a segment is subjected to the initial tube conformation.

2.4. Experimental facts

The spin-lattice relaxation dispersion laws given by equations (2.1)–(2.4) for the Rouse, renormalized Rouse and the tube/reptation models are totally different and highly indicative for any of these formalisms. Actually, experimental evidence for all these models was found under conditions complying with the model assumptions. The frequency dependence predicted on the basis of the Rouse model, equation (2.1), was verified in bulk melts of ‘unentangled’ polymers, i.e. for \( M_w < M_c \) (see [3, 13, 17], [21]–[23]).

Bulk polymer melts above the critical molecular mass, i.e. \( M_w > M_c \) were shown to reproduce the power laws given in equations (2.3) according to the renormalized Rouse formalism [13, 17, 19, 23]. Deviations occasionally occur merely at the highest accessible frequencies corresponding to \( \omega > 1/\tau_e \) when local fluctuations start to dominate. For short enough polymers with molecular masses in the range \( M_c < M_w < 20 000 \), a low-frequency plateau may show up in the experimental frequency window, \( 10^3 < \omega < 3 \times 10^9 \) rad Hz, due to the cut-off provided by component C (see [13]). This phenomenon reflects the terminal relaxation of the polymer chains and the final loss of any memory to the initial conformation.
In spite of the fact that the tube/reptation model was originally proposed for the description of bulk-entangled polymers, the limits given in equation (2.4) could never be verified experimentally in samples of any polymer species. To be strictly correct, it should be mentioned that de Gennes, in his first reptation paper [20], explicitly restricted the validity of his formalism to systems with ‘fixed obstacles’, whereas Doi and Edwards later assumed a fictitious tube representing chain entanglements [10]. The conclusion is that this fictitious tube in reality does not have the property of ‘fixed obstacles’.

However, such a scenario can be established experimentally by confining mobile linear polymer chains in narrow pores of a solid matrix. Under such conditions, all predictions of the tube/reptation model turned out to be perfectly valid [1]–[4], [8, 13]. The length scale of the pore diameters was in the range between 1 and 100 nm. Figure 1 shows typical electron micrographs of the system we are mainly referring to. In this sort of sample, deuterated or undeuterated linear polyethylene oxide melts are confined in pores of a quasi-rigid methacrylate matrix. The Doi–Edwards limit (II)DE given in equation (2.4), which is particularly characteristic for reptation, was verified to be in perfect compliance with the theory.

The system under consideration is linear polyethylene oxide (PEO) strands embedded in a solid methacrylate matrix, i.e. polymers are confined in a polymer matrix prepared by a spinodal demixing technique [7, 8]. In this way, wall adsorption effects are avoided which otherwise may influence the dynamic behaviour as demonstrated in [24] with polymers in a porous silica glass. The data referred to in the present paper do not indicate any influence of adsorption.

The conformations of the PEO chains and of the strands in which they are confined are assumed to be Gaussian, i.e. the distributions of the end-to-end distances comply to Gauss functions. The cross-section of the strands is roughly circular (see figure 1). This is however of minor importance since the spin-lattice relaxation features considered here refer to root-mean-square segment displacements of only 1–10 nm. The cross-sectional shape of the strands therefore does not matter on the time scale of the experiments referred to.

The interfacial tension between PEO strands and methacrylate matrix is also assumed to be of negligible influence. The parameter crucial for the corset effect to be discussed in the following is the isothermal compressibility. Interfacial tension will not affect the liquid specific value of this quantity perceptibly apart from the fact that we are dealing with an order of magnitude estimation.

Figure 2 shows experimental frequency dependences of the spin-lattice relaxation time in PEO melts under conditions corresponding to the premises of all three model theories mentioned above. ‘Unentangled’ bulk PEO melts of molecular mass $M_w = 1665 < M_c$ can be described by equations (2.1) and (2.2) for the Rouse model.

‘Entangled’ bulk PEO melts with molecular mass $M_w = 10170 > M_c$ show a $T_1$ dispersion according to a power law $T_1 \propto \omega^{0.33}$, corresponding to region II given in equation (2.3) as expected for the renormalized Rouse formalism. The low-frequency crossover to region III, which was observed in experiments for much longer PEO chains [13, 17, 22], is concealed by the occurrence of a ‘component C’ cut-off plateau expected to show up in the experimental frequency window for low molecular masses. At the highest frequencies some influence of local segment fluctuations appears to become visible.

Confining the same polymers in pores with diameters ranging from 8 to 58 nm significantly changes the $T_1$ dispersion behaviour irrespective of whether the molecular mass is below or above the critical value in the bulk polymer. The peculiar prediction given in equation (2.4) for limit (II)DE is well verified by the experimental result $T_1 \propto M_w^{0.75} \omega^{0.75}$ in a wide frequency range both
Figure 2. Experimental verification of the three model theories under discussion in this study: frequency dependence of the proton spin-lattice relaxation times of linear PEO in bulk and confined in porous methacrylate samples at 85 °C. The molecular masses of PEO were \( M_w = 1665 \) and 10 170. The data for PEO 1665 and PEO 10 170 are represented by open and filled symbols, respectively. The pore diameters of the different methacrylate samples were evaluated from NMR diffusometry data [8] to be 8, 13, 21, 33 and 58 nm. The PEO 1665 data refer to a pore diameter of 8 nm. The proton signal of the matrix was negligible under the experimental conditions. The data at 200 and 400 MHz have been recorded with conventional high-field NMR spectrometers. The low-frequency \( T_1 \) values slightly increase with increasing pore diameter consistently. The upper solid curves were fitted to the experimental data of bulk PEO 1665 using equations (2.1) and (2.2) predicted for the Rouse model with some influence of local segment dynamics (‘component A’). The fitted parameters are \( \tau_s = 4.7 \times 10^{-11} \text{s} \), \( C_1 = 7.1 \times 10^9 \text{s}^{-2} \), \( C_2 = 3.5 \times 10^8 \text{s}^{-2} \), \( C_1^* = 5.2 \times 10^9 \text{s}^{-2} \), \( C_2^* = 1.5 \times 10^9 \text{s}^{-2} \). The straight lines representing power laws refer to predictions by the renormalized Rouse theory and the tube/reptation concept.

for proton and deuteron relaxation [1, 3]. The plateau seen at low frequencies is attributed to the failure of the standard Bloch–Wangsness–Redfield relaxation theory to account for situations, where correlation times are getting longer than the spin-lattice relaxation time [6]. This plateau also conceals the crossover to limit (III)DE so that this dispersion region is not reflected by the experimental data so obviously.

The model theories referred to in this paper, namely the Rouse model, the renormalized Rouse theory and the tube/reptation concept evidently find their experimental counterparts in the data shown in figure 2 for bulk untangled, bulk entangled and confined dynamics conditions in that sequence. The most striking finding, however, is the fact that the confined dynamics essentially does not depend on the pore diameter between 8 and 58 nm. This finding was termed the ‘corset effect’ [3]. A series of samples was prepared in this pore diameter range [8] to detect any confined-to-bulk dynamics crossover which obviously does not occur although the largest
Figure 3. Schematic illustration of the tight tube of diameter $d$ effective for reptation of polymer chains confined in a pore of diameter $d_{\text{pore}}$ as a consequence of the corset effect.

The pore diameter is 15 times larger than the Flory radius of PEO 1665. Larger pore diameters would certainly be desirable but cannot be prepared at the present state of the art. One is thus left with the task first to explain the weak influence of the pore dimension on chain dynamics and second to estimate the critical pore diameter at which the crossover to bulk dynamics can be expected.

3. Estimation of the effective tube diameter

In the following we distinguish the ‘pore diameter’ $d_{\text{pore}}$ and the ‘tube diameter’ $d$ effective for reptation. We will first discuss the narrow pore limit, where the pore diameter $d_{\text{pore}} \ll R_F = bN^{1/2}$ is much smaller than the Flory radius of the confined polymer consisting of $N$ Kuhn segments of length $b$. Of course, the Flory radius in this case is supposed to be taken under bulk conditions. The pore geometry is assumed to be a cylinder of diameter $d_{\text{pore}}$ (see figure 3). Under such conditions, the polymer chain will necessarily have a stretched conformation that can be considered as a linear sequence of ‘blobs’ of diameter $d_{\text{pore}}$. Inside these blobs, a Gaussian (i.e. random coil) chain conformation can be assumed. The number of Kuhn segments per blob and chain is estimated to be

$$n_{s,\text{blob}} \approx \frac{d_{\text{pore}}^2}{b^2}.$$  (3.1)

Consider now a section of the cylindrical pore of an axial length of the order $d_{\text{pore}}$. The total number of Kuhn segments in this section is of the order

$$N_{s,\text{section}} \approx d_{\text{pore}}^3 \rho_s,$$  (3.2)

where $\rho_s$ is the number density of Kuhn segments. The number of different polymer chains populating the pore section is consequently

$$n_{p,\text{section}} \approx \rho_s d_{\text{pore}}^3/n_{s,\text{blob}} = \rho_s b^2 d_{\text{pore}}.$$  (3.3)

Since the pore walls are assumed to be impenetrable, the diffusional degree of freedom of polymer chains is to reptate along the cylinder. The tube effective for reptation generally speaking need not be identical to the confining pore. To take this possibility into account, we
assume $d \leq d_{\text{pore}}$ for the diameter effective for reptation. We will now estimate the order of magnitude of the effective tube diameter $d$.

The chain section forming a blob of size $d_{\text{pore}}$ can be subdivided into a series of small blobs of diameter $d$. Since a Gaussian chain conformation is assumed on the length scale of the large blob, the number of small blobs on the chain section in a large blob is

$$n_{b, \text{section}} \approx \frac{d_{\text{pore}}^2}{d^2}. \quad (3.4)$$

The number of Kuhn segments of one chain in a small blob is of the order

$$n_{s, \text{small blob}} \approx \frac{d^2}{b^2}. \quad (3.5)$$

We will consider now the well-known thermodynamic relation for the mean-squared fluctuation of the number of particles in a fixed volume $V$ (see e.g. [25]),

$$\langle n^2 \rangle - \langle n \rangle^2 = k_B T \rho_s \kappa_T \langle n \rangle, \quad (3.6)$$

where $\langle n \rangle$ is mean particle number in $V$, $k_B$ the Boltzmann constant, $T$ the absolute temperature and $\kappa_T$ the isothermal compressibility of the polymer melt. Equation (3.6) can be rewritten for a chain section in a large blob of linear dimension $d_{\text{pore}}$ as

$$\langle N_{s, \text{section}}^2 \rangle - \langle N_{s, \text{section}} \rangle^2 \approx d_{\text{pore}}^3 \rho_s k_B T \kappa_T. \quad (3.7)$$

Note that this is an approximate equation in contrast with equation (3.6) since equation (3.2) represents only an order of magnitude estimation.

The right-hand side of equation (3.7) can also be estimated in a different way. As outlined above, the polymer chains reptate each in its own tube. This means that the fluctuations of the number of Kuhn segments in different tubes can be considered as independent. Similarly the number fluctuations of Kuhn segments in different small blobs of a chain can also be assumed to be independent. The chain sections located in small blobs have approximately a Gaussian conformation and can, therefore, be considered as a strongly fluctuating system (see e.g. [26, 27]). The consequence is

$$\langle N_{s, \text{section}}^2 \rangle - \langle N_{s, \text{section}} \rangle^2 \approx n_{p, \text{section}} n_{b, \text{section}} n_{s, \text{small blob}}^2. \quad (3.8)$$

Using equations (3.3)–(3.5), we find, for the relation in equation (3.8),

$$\langle N_{s, \text{section}}^2 \rangle - \langle N_{s, \text{section}} \rangle^2 \approx \rho_s d_{\text{pore}}^3 d^2 / b^2. \quad (3.9)$$

The comparison of equations (3.7) and (3.9) leads to the following expression for the effective tube diameter:

$$d \approx \sqrt{b^2 \rho_s k_B T \kappa_T}. \quad (3.10)$$

The quantity

$$p = \left( b^2 \rho_s \right)^{-1} = N \rho_s^{-1} / N_b^2 \quad (3.11)$$

is the so-called packing length (see e.g. [28]). The packing length is, by definition, the ratio of the chain volume and the squared Flory radius; qualitatively, it characterizes the typical distance
between nearest Kuhn segments on different polymer chains. In melts of flexible polymers, the packing length is in the range $p = 0.17–0.4$ nm [28]. In terms of the packing length, equation (3.10) takes the form

$$d \approx \sqrt{k_B T \kappa_T / p}.$$  

(3.12)

Typical values for the compressibility of polymer melts at room temperature are of the order $\kappa_T = 10^{-11}–10^{-10}$ m$^2$ N$^{-1}$ [29]. The effective tube diameter is therefore expected to be only of the order

$$d \approx 0.5 \text{ nm.}$$  

(3.13)

4. The confined-to-bulk dynamics transition

The transition from reptation dynamics in an effective tube due to the corset effect to bulk dynamics is expected when the diameter of the cylindrical pore $d_{\text{pore}}$ becomes sufficiently larger than the Flory radius of the polymer in bulk melts, $R_F = bN^{1/2}$. In the following, we estimate the condition for this transition in terms of the ratio $d_{\text{pore}}/R_F$.

Consider a polymer chain having its centre of mass at a distance of the order of $R_F/2$ apart from a pore wall. There will be many positions where the chain touches the pore wall (see figure 4 for an illustration). The question now is: what is the mean distance between neighbouring contact points (‘temporal wall knots’)?

We simplify the consideration by assuming a planar wall geometry. A Gaussian random coil consisting of $N$ Kuhn segments of length $b$ has a spatial extension of order $bN^{1/2}$. The random coil is now supposed to be intersected by $N^{1/2}$ parallel planes of nearest-neighbour distance $b$. The total number of segments crossing these planes is of order $N$, i.e. each plane is on average contacted $N/N^{1/2} = N^{1/2}$ times by the polymer coil. The same number of contacts is expected
for a chain with a centre of mass separated $R_F/2$ apart from the wall. The chain section between two neighbouring contacts thus contains $N/N^{1/2} = N^{1/2}$ Kuhn segments, i.e. the linear distance between nearest-neighbour contacts is of the order $bN^{1/4}$.

If the ratio $d_{\text{pore}}/R_F$ is not large enough, the corset effect may still apply, i.e. the polymer chains reptate in their own tight tubes of diameter $d$ as estimated above. The pore wall and the chain sections between two nearest contacts form ‘temporal wall knots’ (see figure 4). Chains entangling such temporal wall knots suffer constraints by the knots due to the impenetrability of pore walls and the uncrossability of the knot-forming polymer chain. The mean lifetime of a knot is of the order $\tau_s N^3$, which is the time needed for a chain of $N$ Kuhn segments to escape from the initial effective tube via reptation [10].

The transition from confined to bulk dynamics is expected to occur if at least one temporary wall knot of the chain under consideration comes undone. This means that the chain section forming the temporary wall knot gets displaced distances of the order of its initial size, i.e. $bN^{1/4}$, on a time scale much shorter than $\tau_s N^3$. Since the polymer chains are mutually uncrossable, all neighbouring chains in a distance of the same order will be displaced in the same way. The resolution of a temporary wall knot thus demands more or less coherent displacements of $\rho_s b^3 N^{3/4}$ Kuhn segments within a radius of about $bN^{1/4}$. In other words, we are dealing with fluctuations of an ensemble of $\rho_s b^3 N^{3/4}$ Kuhn segments. The thermodynamic condition for such fluctuations, which is the necessary condition for bulk dynamics, is (see equation (3.9))

$$d_{\text{pore}}^3 \rho_s^2 k_B T \kappa_T \gg (\rho_s b^3 N^{3/4})^2,$$

i.e.

$$d_{\text{pore}} \gg \left(\frac{b^3}{k_B T \kappa_T}\right)^{1/3} R_F. \quad (4.2)$$

This is the condition for the confined-to-bulk dynamics transition. Equation (4.2) suggests that bulk behaviour of chain dynamics can only be expected if the diameter of the confining pores is large enough relative to the Flory radius. The non-trivial result is the form of the prefactor $(b^3/k_B T \kappa_T)^{1/3}$, which indicates that the confined-to-bulk dynamics transition depends on the compressibility of the polymer melt. For typical values $b \simeq 1 \text{ nm}$, $\kappa_T = 10^{-11} - 10^{-10} \text{ m}^2 \text{ N}^{-1}$ and at room temperature, we estimate

$$d_{\text{pore}} \gg 10 R_F. \quad (4.3)$$

5. Discussion

Nuclear magnetic relaxation dispersion experiments suggest that polymer melts confined in solid matrices with nanoscopic pores strictly follow reptation dynamics irrespective of the molecular mass, whereas the same polymers in bulk obey Rouse dynamics for $M_w < M_c$ and renormalized Rouse dynamics for $M_w > M_c$ on the time scale of nuclear magnetic relaxation. Predictions of any of these model theories were effectively reproduced in numerous experiments by ensuring that the experimental conditions corresponded to the model premises.

A rather striking finding was that pore confinements stipulate reptational dynamics even for pore diameters exceeding the bulk Flory radius. The ‘tube’ diameter effective for reptation was
estimated to be only a few ångströms, which is close to the nearest polymer–polymer distance. This ‘corset effect’ was shown to be a consequence of the combined effect of impenetrable pore walls, the mutual uncrossability of polymer chains and the finite compressibility of polymer melts. Intuitively, it appears to be reasonable that the effective tube diameter $d$ does not depend on the pore diameter $d_{\text{pore}}$ as long as the corset effect applies in full.

For reasons of preparational restrictions the pore diameters of the samples investigated experimentally could be varied only up to about 60 nm. Up to such pore diameters, only little deviation from the corset effect could be observed even for polymers molecular masses as low as $M_w = 1665$. This raises the intriguing question that at what pore dimension the crossover from confined to bulk dynamics, i.e. from reptational to Rouse ($M_w < M_c$) or renormalized Rouse ($M_w > M_c$) dynamics occurs. In the present study, we have estimated the critical pore diameter to be much larger than 10 times the Flory radius. From this point of view, it becomes clear that the crossover could not be unambiguously monitored with the samples available in our experiments.

The above treatment predicting the corset effect in accordance with experimental findings is to be regarded in contrast with the conventional tube/reptation model often assumed for the description of ‘entangled’ polymer melts [10, 27]. In that phenomenological tube/reptation model, the ‘tube’ is anticipated in the form of a postulate and is not derived employing microscopic arguments. The tube diameter was suggested by Doi and Edwards to be given by $d_{\text{DE}} = b N_e^{1/2}$, where $N_e$ is the number of Kuhn segments between ‘entanglements’ [10] irrespective of what the term meant. Actually it is a parameter of phenomenological nature that needs to be fitted to experimental data of the viscoelastic plateau of polymer melts. For melts of flexible macromolecules this fitting parameter was reported to adopt values in the range $d_{\text{DE}} \simeq 5$–7 nm in contrast with the tube diameter of 0.5 nm suggested by our microscopic formulae given in equations (3.10) or (3.12). Note that these equations have been derived using quite general arguments and, hence, should be valid also for bulk melts if reptation is the dominating process. Since experimental data contradict the tight tubes predicted by the microscopic treatment of equations (3.10) and (3.12), we conclude that polymer-chain dynamics in bulk melts is much more complicated than that anticipated by Doi and Edwards.

If the corset effect applies, i.e. if the limit for the pore diameter given in equation (4.3) is not valid, reptational dynamics is visible. As outlined above, polymer chains reptate along their own contour in a tight tube, the width of which corresponds to the nearest-neighbour distance. In the opposite limit, i.e. effectively in bulk melts, the argument leading to the prediction of the corset effect fails, and reptation cannot be regarded as a mechanism dominating chain dynamics on the time scale of spin-lattice relaxation dispersion.

The prefactor $(b^3/k_BT\kappa T)^{1/3}$ given in inequality (4.2) reflects the fact that the confined-to-bulk dynamics transition is determined not only by the pure geometrical constraints in terms of the pore diameter $d_{\text{pore}}$ and the Flory radius of the macromolecules in bulk, $R_F$. The most crucial quantity is rather the compressibility which determines the ability of the system to fluctuate with respect to segment number density or, in other terms, with respect to free volume needed for conformational rearrangements by chain modes. The impenetrable pore walls furthermore act as a kind of ‘corset’ preventing excessive free volume fluctuations and thus any chain modes other than reptation in effectively tight tubes of a diameter corresponding to the nearest-neighbour distance of polymer chains. The natural basis of the corset effect thus is (i) the low compressibility, (ii) the uncrossability of polymer chains and (iii) the impenetrability of the pore walls with pore diameters not fulfilling the inequality (4.2). If any of these properties were absent, the corset effect could not arise, and chain dynamics would tend towards bulk behaviour.
In [30, 31], long-range interactions of the order of 10 times the radius of gyration were reported for perfluorinated polyether confined between two mica surfaces. Most probably this is also a consequence of the corset effect discussed in the present study.

Our results appear to be important also for the appropriate interpretation of computer simulation studies of entangled polymer dynamics. Numerous computer simulations have been carried out with the goal to understand the Rouse/reptation transition in polymer melts [32]–[37]. An unentangled-to-entangled dynamical transition was definitely shown, and some findings indicate reptation features. In the light of the corset effect discussed here, this is not unexpected. In any computer simulation periodic boundary conditions must be employed to account for the finite system size determined by the limited computer capacity, i.e. the number of polymer segments in the probe volume of such simulations is not subject to fluctuations. Therefore, the anticipated situation is analogous to a polymer melt confined in a kind of pore. The pore diameter $d_{\text{pore}}$ in our treatment corresponds to the dimension $d_{\text{sim}}$ of the simulated system. If this system size does not satisfy inequality (4.2) or (4.3), the periodic boundary conditions unavoidably mimic reptation-like motions as a sort of artificial ‘corset’ effect. It therefore appears that computer simulations render confined rather than bulk dynamics. Actually the possibility of finite size effects and an influence of the periodic boundary conditions on the simulated properties have been discussed several times in the literature. Note however that these discussions mainly referred to static properties of polymer melts anticipating that the quality of simulated static properties entails the same quality of dynamic features. It appears that the elucidation of the corset effect as revealed by spin-lattice relaxometry and analytically discussed in the present paper will have a strong impact on numerical investigation methods.

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