Comparison of Various Correlation Times in Polymer Melts by Molecular Dynamics Simulation

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Abstract. This investigation presents data from prolonged molecular dynamics simulations of dense monodisperse polymer melts of linear polymer chains of length between \( N = 3 \) and \( N = 255 \). Here \( N \) is number of chain coarse-grained segments. The study aim is to observe the crossover from Rouse-like dynamics for short chains to reptation-like dynamics for long chains and its influence on various translational and orientational correlation times. To address the problem, we calculate a variety of different quantities: standard mean-square displacement of inner monomer and of the chain mass centre, autocorrelation function of chain end-to-end vector, orientational autocorrelation functions of segment and chain end-to-end vector. The last two functions define NMR relaxation in polymer melts. The chain length dependences of all large-scale correlation times reveals clear crossover from non-entangled to entangled dynamics near \( N_C \approx 35 \). Additional primitive path analysis of the same data gives statistically consistent entanglement value \( N_E \approx 14 \), i.e., the longest chain investigated is well entangled and displays explicit motional anisotropy. The full data assembly explains qualitatively strong dependence of NMR transverse relaxation time for Rouse-like regime and weak one in reptation regime.

1. Introduction
Phenomenological theory of polymer chains dynamics [1, 2] is used very long time to interpret data of natural [3] and simulated experiments [4-7] and it is undoubted in all basic statements. But quantitative agreement of its statements with experimental data was observed rarely because it had been formulated for ideal chains of infinite length with Gaussian structure. In other words the surrounding chains are treated as a fixed network of impenetrable obstacles. The infinite chain length approximation is very difficult to realize in all kind of experiments. The most part of such experiments is based on the analyses of the mathematical consequences of the fact that chain motion is reptation-like one [1], i.e. it is characterized by strong space anisotropy of chain diffusion along and perpendicular to the contour of a “tube” or “primitive path” which is formed by surrounding chains.

The term “primitive path” had been abstract definition a long time till recent paper [8] in which an algorithm for primitive path finding had been suggested. This algorithm permits to check primary concept of the polymer dynamics, in other words to find quantitative degree of the chain diffusion anisotropy. This concept had been checked some times [9-13] by Monte Carlo simulation and the authors of the works [9-11] had concluded that tube was not needed to observe all time regimes of long chain diffusion. The more, an alternative phenomenological theory of polymer dynamics had been suggested.
[11] to explain such the contradiction. The chain diffusional anisotropy revealed in the works [12, 13] was very weak and not enough for reptation regime.

The recent experiments had used complicated methods of samples preparation to create additional artificial tube for real macromolecules. For example, an embedding of real macromolecules into mesoscale cylindrical pores enhanced the space anisotropy of macromolecule diffusion according to the analysis of spin lattice relaxation dispersion [14, 15]. Thermodynamic restriction of the basic notions of the reptation theory had been discovered as the result of these experiments [15].

The aim of this study is scaling analysis of chain diffusion as function of its length and demonstration of simultaneous existence of the tube and indistinct visualization of time diffusive regimes concluded from this constraint. For this purpose the investigation of the crossover from Rouse-like dynamics for short chains to reptation-like dynamics for long chains had been made by protracted molecular dynamics simulation. The crossovers were observed for variety of translational and rotational chain motion each of which is characterized by its proper correlation time. The total collection of the data is applied to explain qualitatively chain length dependence of the NMR transverse relaxation time in polymer melts.

2. Model and simulation technique
A system of spherical particles, i.e., beads or monomers of mass $m$ is modeled in three-dimensional $NVT$, canonical, ensemble [16] to observe chains motion. Non-bonded interaction $\varepsilon_P$ between beads on distance $r$ is described by simple truncated and repulsive Lennard-Jones pair potential with length parameter $\sigma$ [16, 17]:

$$
\varepsilon_P(r) = \begin{cases} 
4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 + \frac{1}{4} \right], & r < r_C \\
0, & r \geq r_C, \quad r_C = r_{EQ} = 2^{1/6}\sigma 
\end{cases}
$$

Here, $\varepsilon = k_B T$ is depth of potential deep at the equilibrium distance, $r_{EQ}$, reduced to mean thermal energy, $k_B T$; $r_C$ is cut-off distance for conventional reducing of computation. Conventional dimensionless set of parameters $m = \varepsilon = \sigma = 1$ defines all other system units including time unit

$$
\tau_0 = \sigma \sqrt{\frac{m}{\varepsilon}} = 1.
$$

Diffusion unit is $\sigma^2/\tau_0$. The cubic volume of the system with side length from 20 to 32 is limited by periodic boundary conditions [16, 17]. Main system parameter is pack coefficient, 0.50, defined as system volume part occupied by beads, the corresponding reduced bead density is 0.96. Such the parameters describe condensed substance in liquid state [17]. Bonded neighbor beads in a chain interact through a finitely extensible non-linear potential [17], which does not prevent their overlap:

$$
\varepsilon_B(r) = -15 \cdot \left( \frac{\tau_0}{\sigma} \right)^2 \cdot \varepsilon \cdot \ln \left\{ 1 - \left( \frac{r}{\tau_0} \right)^2 \right\}, \quad \tau_0 = 1.5 \cdot \sigma.
$$

Equations (1) and (3) define so-called Kremer-Grest coarse-grained chain with well-known properties for a few lower melt density, 0.85, and altogether with chosen cut-off distance realize for isolated chains good solvent conditions [17]. This coarse-grained chain has not small-scale rotational motion around bonds each of which corresponds to the chain segment. All simulated polymer melts consist of $n_{CH}$ chains with $(N+1)$ beads or $N$ segments, where $N$ is ranged from 3 to 255. General number of beads in the system is $n = (N+1) n_{CH}$ and varied from 8 000 to 32 768 for 22 chains of various length. Ratio of the system linear size to the chain mean-square gyration radius was varied from 4 to 20.

Numerical integration of the bead motion equations is made by velocity Verlet algorithm with constant time step $0.01 \cdot \tau_0$, the temperature was kept constant by coupling the motion to Nose-Hoover
thermostat [12, 18, 19] where the coupling constant is essentially less than unity. The coupling constant smallness implies minor stochastic perturbation of the system dynamics which is originally deterministic one. Additionally the system dynamics is periodically corrected by subtraction of its mass centre velocity from the velocities of all beads [17]. As a result the simulation algorithm permits to observe the system evolution during unlimited long time providing temperature fluctuations no more than 0.001 and stationary Maxwell’s distribution of beads velocities in any point of phase trajectory. The last characteristic was checked occasionally, for example, for trajectory of length \(2 \cdot 10^8\) integration steps per \(5 \cdot 10^6\) steps.

Pre-equilibration of all investigated melts was made before the phase trajectory storage because polymer dynamics theory conclusions are applicable only to the chains in thermodynamically equilibrium conformation. This problem is impotent in a simulation experiment [17, 20] and realized in this study following way. The first, a system of chains of necessary length is designed in crystal state. The second, the system is evolved in Rouse phantom regime till reaching conformational equilibration. The algorithm performance in phantom regime approximately 1000 time more than in excluded volume regime and equilibration is very quick. The third, slow introduction of the increased excluded volume potential is made, taking care that in the beginning the chains can easily cross each other. The increasing excluded volume potential makes local reconstruction of the melt. This process needs bead displacement on its size only, i.e., it is local one and also sufficiently quick. Such the procedure is made for system of one size only one time because equilibrated short chains can be easily got from equilibrated long chains by there breaking with sequential short-time equilibration.

3. Properties of the simulated melt

3.1. Theoretical characteristics of the chain translational and rotational motion

Important quantities used to study the crossover from Rouse to reptation dynamics are the following mean-square displacements [2, 3, 7, 17]:

\[
\begin{align*}
g_1(t) &= \langle [\mathbf{r}_{N/2}(t) - \mathbf{r}_{N/2}(0)]^2 \rangle \\
g_{1C}(t) &= \langle [\mathbf{r}_{N/2}(t) - \mathbf{r}_{N/2}(0) - \mathbf{r}_{CM}(t) + \mathbf{r}_{CM}(0)]^2 \rangle \\
g_{CM}(t) &= \langle [\mathbf{r}_{CM}(t) - \mathbf{r}_{CM}(0)]^2 \rangle \\
g_2(t) &= \frac{1}{2} \langle [\mathbf{r}_N(t) - \mathbf{r}_N(0) + \mathbf{r}_N(t) - \mathbf{r}_N(0)]^2 \rangle
\end{align*}
\]

(4)

Here, \(g_1\) is the mean-square displacement of the middle monomer of a chain (situated at position \(\mathbf{r}_{N/2}(t)\) at time \(t\)), \(g_{1C}\) is the same displacement measured relative to the motion of the chain’s center of mass (\(\mathbf{r}_{CM}(t)\) is position of the center of mass at time \(t\)), \(g_{CM}\) is the mean-square displacement of the chain center of mass, and \(g_2\) is that of the end monomers. To increase statistics \(g_1\) was calculated over 10 % of middle chain beads. Within the framework of the reptation theory for large \(N\) the next asymptotic behavior of mean-square displacement may be expected [2, 3, 7, 17]:

\[
\begin{align*}
g_1(t) &\propto \begin{cases} t^{1/2} \cdot N^0, & t << \tau_E \\ t^{1/4} \cdot N^0, & \tau_E < t < \tau_R \\ t^{1/2} \cdot N^{-1/2}, & \tau_R < t < \tau_D \\ t^{1} \cdot N^{-2}, & \tau_D < t \end{cases} \\
g_{CM}(t) &\propto \begin{cases} t^{1} \cdot N^{-1}, & t << \tau_E \\ t^{1/2} \cdot N^{-1}, & \tau_E < t < \tau_R \\ t^{1} \cdot N^{-2}, & t >> \tau_R \end{cases}
\end{align*}
\]

(5)

(6)
At early times, a chain does not feel the entanglement constraints imposed by its neighbors. Assuming the Rouse model to provide a realistic description for non-entangled chains, it’s expected \( g_1(t) \propto t^{1/2} \) and \( g_{\text{CM}}(t) \propto t \) in this case. If \( t \) equals the entanglement time, \( \tau_E \), the constraints begin to dominate the polymer dynamics. For larger times, a chain moves as if it were confined in a tube created by its neighbors. It can only slide along the tube axis or primitive path, whereas motion perpendicular to the tube is suppressed. Since the tube can be thought of as an envelope around the chain’s random-walk-like configuration, the chain performs Rouse dynamics along a random walk. This leads to \( g_1(t) \propto t^{1/4} \) and \( g_{\text{CM}}(t) \propto t^{1/2} \). If \( t \) reaches the Rouse time, \( \tau_R \), the chain configuration is relaxed inside the tube. For larger times, the mass center diffuses freely and the middle monomers begin to diffuse out of the tube. The some middle monomers leave the tube completely if \( t \) equals the disengagement time, \( \tau_D \).

For small \( N \) significant corrections of considered regimes must be expected, and all these regimes can be observed clearly only for very large \( N \), where the time scales \( \tau_E \), \( \tau_R \), and \( \tau_D \) are well separated, but it is complicated to reach due to the next relations between the characteristic times \([2, 3, 7, 17]\):

\[
\tau_R = Z^2 \tau_E; \\
\tau_D = 3 \cdot Z \tau_R; \quad Z = (N/N_E) - 1
\]

Here, \( Z \) is the number of entanglements per chain defined by the most impotent and enigmatical parameter of the reptation theory entanglement length, \( N_E \), i.e. mean number of segments between adjacent entanglements along chain. Running ahead, it is useful to notice that the longest simulated chain is characterized by \( Z = 17 \) entanglements.

The value of \( g_{\text{IC}} \) plateau is defined by chain mean-square gyration radius \( R_G^2 \) and permits to find \( \tau_R \) as time of intercept of mass centre mean-square displacement and this plateau according to the definition of \( \tau_R \) \([2]\):

\[
g_{\text{CM}}(\tau_R) = g_{\text{IC}}(t \to \infty) = R_G^2.
\]

Autocorrelation function (ACF) of the chain end-to-end vector \( \mathbf{R}_{\text{EE}} \) is used to describe its rotation quantitatively by rotational time \( \tau_{\text{EE}} \):

\[
C_{\text{EE}}(t) = \langle \mathbf{R}_{\text{EE}}(t) \cdot \mathbf{R}_{\text{EE}}(0) \rangle / [\langle \mathbf{R}_{\text{EE}}(0) \rangle]^2 \approx \exp(-t/\tau_{\text{EE}}).
\]

According to \([2]\) \( \tau_{\text{EE}} \) depends on chain length in the same way as Rouse time:

\[
\tau_{\text{EE}}(N) \propto \tau_R(N) \propto N^x, \quad \begin{cases} 
  x = 2, & N < N_C \\
  x = 3, & N > N_C 
\end{cases}
\]

Here, \( N_C \) is critical chain length which had come into polymer dynamics from multitude of experiments as quantity bordering non-entangled and entangled behavior of polymer melts. Due to this circumstance there are many statistical data for its ratio to \( N_E \), generalized, for example, in work \([21]\):

\[
N_C \approx (1.6 \pm 2.6) \cdot N_E.
\]

The necessity of the wide region may be additionally proved by the well known fact the physical quantity values obtained by various methods are usually differed and should be averaged \([22]\).

### 3.2. The melt structure

To control the degree of polymer melt equilibrium the squared ratio of the chain end-to-end distance to its gyration radius was used. This ratio is the same for phantom chains and for chains with excluded volume from the theory viewpoint \([23]\):
\[
\begin{align*}
\langle R_{EE}^2 \rangle & \approx N^2 \nu b_K^2 \quad (12) \\
\langle R_G^2 \rangle & \approx \frac{\langle R_{EE}^2 \rangle}{6}. \quad (13)
\end{align*}
\]

Here \( b_K \) is the Kuhn segment length, a product of the chain stiffness and mean bond length \( \langle b \rangle \approx 0.95 \cdot \sigma \). The last value is a week function of pack coefficient and got as the result of simulation. \( \nu \) is Flory exponent with theoretical value 0.5 for ideal solution and melt, but may be a slightly more in simulation [7, 23].

3.3. Orientational mobility in the melt

A normalized orientational autocorrelation function (OACF), \( C(t) \), is used as testable experimentally by NMR relaxation. It is defined by the second-degree polynomial, \( P_2(t) \), because spins are considered at beads and constant distance from each other [24]:

\[
C(t) = \frac{\langle P_2(t') \cdot P_2(t'+t) \rangle}{\langle P_2(t') \rangle^2}, \quad P_2(t) = [3\cos^2 \theta(t) - 1]/2 \quad (14)
\]

Here, \( \theta \) is angle of inter-spin vector relative to external constant magnetic field. Fluctuations of some inter-spin vector in time define shape and correlation time, \( \tau \), of the OACF. If OACF is exponential, the \( \tau \) value would be found as

\[
\tau_i = \int_0^\infty C_i(t) \cdot dt. \quad (15)
\]

Index \( i = 1 \div N \) is number of the segments in subunit the fluctuations of which are considered. For example, \( \tau_1 \) means the segment itself and \( \tau_N \) describes reorientation of the chain end-to-end vector. Usual shape of the OACF in simulated melt is sum of undefined number of exponents; therefore \( \tau_i \) was assessed as the OACF decay to 1/e of its initial value. Finally, free induction decay is constructed for the case of incomplete motional narrowing of the NMR absorption line [3, 24]:

\[
M_i(t) = \exp \left[ -\omega_2 \int_0^t (t - \tau) \cdot C_i(\tau) \cdot d\tau \right]. \quad (16)
\]

Here, \( \omega_2 = 1.5 \cdot 10^{-4} \) is the dimensionless second moment of the NMR line in the absence of the molecular motions. It corresponds to complete motional narrowing condition for \( \tau_1 \) and does not correspond to one for \( \tau_N \) for the long chains simulated. Due to non-exponential shape of the free induction decay the effective transverse relaxation time, \( T_2 \), was evaluated the same way as \( \tau_i \).

3.4. Characteristics of the chain reptation

A chain primitive path is the shortest distance between its ends the chain could take without crossing surrounding chains [1] as it is depicted by figure 1. Primitive path is nearly the bent axe of the tube which represents a volume of space that can be explored by a chain without violating the topological constraints. In accordance with this definition Everaers with co-workers [8] had suggested next algorithm to constructing primitive path.

Beads inside a chain are allowed to overlap and decrease in diameter, thus decreasing the contour length of the chain. The intent is to allow chains slowly to shrink their length while maintaining their non-crossability with other chains, until all chains have collapsed onto paths of minimum total length that preserves their original topological interactions. These shrunken chain contours are identified as the primitive paths. In the algorithm, the end beads of all the equilibrated chains are immobilized while the interior beads are allowed to move during concurrent temperature decreasing. Intramolecular excluded-volume effects are turned off while maintaining intermolecular excluded-volume interactions and chains in the system are shrinking simultaneously. This procedure transforms original
$N$ Kuhn segments of length $\langle b \rangle$ of each chain into primitive segments of length $\langle b_{PP} \rangle$. All original beads are also transformed into primitive beads of the same size $\langle b_{PP} \rangle$ due to the algorithm properties. Hence mean contour length of the primitive path is

$$\langle L_{pp} \rangle = N \cdot \langle b_{pp} \rangle .$$  \hspace{1cm} (17)

Each chain entanglement makes primitive path bend, the more number of entanglements the more number of the bends, and the longer primitive path, consisting from straight lines of length $N_E \langle b_{pp} \rangle$ between adjacent entanglements. Considering these lines, strands, as Kuhn segments of Gaussian primitive path we get the number of this segments $(N/N_E)$. Finally end-to-end distance of the original chain can be equalized to the primitive path one:

$$\langle R_{EE}^2 \rangle = N \cdot N_E^{-1} \cdot \langle (N_E b_{pp})^2 \rangle = N_E \cdot N^{-1} \cdot \langle L_{pp} \rangle^2 .$$  \hspace{1cm} (18)

Hence we are able to find number of beads per entanglement length and primitive path contour length:

$$N_E = N \cdot \langle R_{EE}^2 \rangle \cdot \langle L_{pp} \rangle^{-2} , \quad \langle L_{pp} \rangle^2 = N \cdot N_E^{-1} \langle R_{EE}^2 \rangle .$$  \hspace{1cm} (19)

Equation (19) relates all primitive path characteristics to the ones of the original chain. Though its derivation is based on Gaussian statistics for long chain the formula may be applied to the chain of any length. For example, primitive path of short chain without entanglements is straight line and $L_{PP} = R_{EE}$.

Substitution of this equality into equation (18) gives result with simple physical significance $N_E = N$. In other words, $N_E$ is monotonically increasing function of the chain length for melt below $N_C$.

If the chain moves along the tube, there should be substantial memory of the primitive path configuration, at least for some middle chain segments. Thus, the following procedure has been applied in order to extract the longitudinal or axial, $g_A$, and transverse or normal, $g_N$, components of the chain motion \cite{2, 9, 13}. Figure 2 schematically depicts two primitive paths, $AB$ and $A_1B_1$, of the same chain at time 0 and $t < \tau_R$. Let $i$-th primitive path bead with coordinates $r_i(0)$ has displaced in position $r_i(t)$ at $A_1B_1$, and the nearest neighbor to its original position is appeared $k$-th primitive path bead with coordinates $r_k(t)$. The space displacement $\Delta r_i(t)$ may be resolved into axial, $\Delta r_A(t)$, and normal, $\Delta r_N(t)$, components. The axial component is defined as

**Figure 1.** Schematic representation of the chain and its coarse-grained characteristics.

**Figure 2.** The same primitive path in time moments 0, $AB$, and $t$, $A_1B_1$: resolution of the $b_{pp}$ displacement into axial and normal components.
\[ \Delta r_a = |i - k| \cdot \langle b_{pp} \rangle. \] (20)

If difference of the beads number is more than \( N_E \) the axial component becomes curvilinear and more than its total space displacement, which is equal to the vector sum
\[ \Delta r_i(t) = \Delta r_{r_i}(t) + \Delta r_a(t). \] (21)

Raising to the second power both sides of this equation and suggesting statistical independence of the components \([14, 15]\) we get equation for the middle bead mean-square displacement in the space of the primitive paths:
\[ g(t) = g_{N}(t) + g_{A}(t). \] (22)

In accordance with the definition (19) \( g_A \) cannot be more than a quarter of the primitive path squared length, and then it gets plateau and loses its original sense. Combination of the equations (12), (13), and (19) gives the plateau value
\[ g_{A}(t \geq \tau_R) = \left( \frac{L_{pp}}{2} \right)^2 = \frac{3}{2} \frac{N}{N_E} R_G^2 = \frac{3N^{2\nu+1}b_K^2}{2N_E}. \] (23)

Time of the plateau achieving in equation (23) is defined by the chain exit from its tube after \( \tau_R \). It is seen the plateau value is higher than \( g_{1C} \) plateau, \( R_G^2 \), and dependent on chain length approximately quadratically.

Quantitative characteristic of the chain diffusion anisotropy, \( a(t) \), is made by the ratio of normal and axial mean-square displacement \([9-12]\):
\[ a(t) = g_{N}(t)/g_{A}(t). \] (24)

Isotropic diffusion is characterized by \( a(t) = \text{const} = 2 \) in region of its definition which is very short in time. When chain diffuses in the tube of diameter \( d_T \) \([2, 3]\)
\[ d_T^2 = N_E^{2\nu} \langle b_K^2 \rangle = N_E^{2} \langle b_{pp}^2 \rangle, \] (25)

its normal displacement is no more than half of the diameter \([14]\) and shouldn’t depend on chain length after \( N > N_C \). The axial displacement should increase in time till asymptotic value, equation (23), growing with chain length. Substitution of equations (17) and (25) into equation (24) for the moment of exit from the tube, \( t = \tau_A \), gives diffusional anisotropy observed:
\[ a(\tau_A) = \left( \frac{d_T}{2} \right)^2 / \left( \frac{L_{pp}}{2} \right)^2 = \left( \frac{N_E}{N} \right)^2 = \frac{1}{(Z-1)^2}. \] (26)

It is seen that the anisotropy should be less than unity and decreased as squared number of entanglements per chain. To characterize the \( a(t) \) minimum the time \( \tau_A \) was introduced because its physical significance differs from \( \tau_R \) one. Namely, \( \tau_A \) means persistent contact time of the Rouse chains with surroundings and the entangled state life time of the reptating chains in the melt.

4. The simulated results and discussion

4.1. Time dependence of the chain diffusional characteristics
Translational and rotational mobility of the chains and their segments in the melt are characterized by typical dependences which are shown in figures 3 and 4 for the chain of 127 segments length. Dynamics of all length chains is observed in the time region \((10^5\div10^6)\) \( \tau_R \) to define the largest characteristic times \( \tau_{KE} \) and \( \tau_R \) marked by vertical arrows. Horizontal arrow \( R_G^2 \) marks \( g_{1C}(t) \) plateau, curve 3 in figure 3, the interception of which with \( g_{CM}(t) \), curve 1, gives \( \tau_R \). The decay of the end-to-end vector
ACF, curve 1, in figure 4, permits to find $\tau_{EE}$ which is close to $\tau_R$ for this chain length. Value of $\tau_E$ is marked according to the assessment mentioned below such as the horizontal dotted line $(d_T/2)^2$ assessed by equation (25). The intersection of these two lines in figure 3 has to mark the regime change of curve 2, but the changing is unnoticeable. The free diffusive limit for $g_{CM}(t)$, curve 1 in figure 3, is also not achieved therefore chain diffusion coefficient is not defined and discussed.

Figure 3. Time dependence of mean-square displacement for chain of length 127 segments: chain mass center (1), middle bead (2), middle bead relative to the mass center (3); ratio of the mean-square displacement of the end bead and the middle bead (4) in linear scale. Arrows $R_G^2$ and $\tau_R$ show their estimation. Dashed lines $(d_T/2)^2$ and $\tau_E$ are superposed from other figures.

Figure 4. Time dependence of the segmental (1) and chain (2) OACF, the chain end-to-end vector ACF (3) for chain of length 127 segments. Arrows $\tau_1$, $\tau_N$, and $\tau_{EE}$ show their estimation. Dashed line $\tau_E$ is superposed from other figure.

Curve 4 in figure 3 shows ratio of the mean-square displacement of the end bead, $g_2(t)$, and the middle bead, $g_1(t)$, in linear scale.

The power laws of equation (5) and (6) are observed in figure 3 only approximately because they describe the asymptotic behavior and can be observed clearly only for very large $N$, where the time scales $\tau_E$, $\tau_R$, and $\tau_D$ are well separated. For smaller $N$, significant deviations have to be expected as it has been demonstrated by a detailed theoretical analysis and simulation [25]. The coarse-grained model is not satisfied this condition, since the subchain units corresponding to various time scales are very close in sizes.

The main information from figure 4 is relation between segmental, curve 1, and chain, curve 2, OACF. It is seen the noticeable decay of the chain OACF is in the time region where the segmental OACF shape is hidden by noise. I.e., contribution of the orientation of the chain as a whole is not impossible to extract from the segmental OACF for the data system discussed.

The collection of the dependences as in figures 3 and 4 for other length chains differs only by values of characteristic times and conservers the same forms. Therefore integrated analysis of all characteristic times will be made latter as chain length dependences.

The similar analysis is made for mean-square displacements in the primitive path space, the example of which is depicted in figure 5 for the same length chain. The axial and normal mean-square displacements of the chain middle monomer are represented by curves 1 and 2, respectively. Both mean-square displacements increases monotonically till $\tau_R$. The axial one approaches plateau after $\tau_R$, the normal one begins to increase faster after this time. These facts are caused by going out of the applicable domain according to the equation (23). The normal mean-square displacement should have plateau
due to limitation by the tube radius and its absence is also explained by earlier going out of the applicable domain.

The ratio of the normal mean-square displacement to the axial one, curve 3, is appeared as wide minimum with plateau in its central part. The deepest and the most right point of the plateau is marked by arrows and represents the time, $\tau_A$, and value, $a(\tau_A)$, of the anisotropic diffusion: for this curve $a(\tau_A) \approx 0.1$. The horizontal dashed lines are carried over from other figures to compare the mean-square displacement scales. The axial mean-square displacement plateau, curve 1, is not reached yet, but it is seen that its value should be sufficiently higher $R_G^2$ in accordance with equation (23).

\[ \text{Figure 5. Time dependence of various reptation characteristics for chain of length 127 segments: mean-square displacements of the middle bead relative to the tube in the axial (1) and normal (2) directions, and ratio of the second one to the first one (3). Arrows $\tau_A$ and $a(\tau_A)$ show their estimation. Dashed lines $R_G^2$, $(d_T/2)^2$, $\tau_E$, and $\tau_R$ are superposed from other figures.} \]

4.2. Static properties of the chain

Figure 6 depicts dependence of the chain mean-square gyration radius, $R_G^2$, on the chain length with asymptotic power law $2\nu \approx 1.07$. Data processing according to the equations (12) and (13) gives Kuhn segment length $\langle (b_K)^2 \rangle \approx 1.20$. The large circles along the dependence 1 are mean-square gyration radii of the various subunits of the longest chain simulated, 255 segments. The coincidence with the curve demonstrates that the subunit conformation inside the chain repeats the conformation of the same length free chain. It indicates all chains of the simulated melts were in thermodynamic equilibrium what is not always obtainable in simulation of long chains [20].

\[ \text{Figure 6. Dependence of mean-square gyration radius (1) and Rouse time (2) on chain length. The large circles are } R_G^2 \text{ of the various sub-units inside the chain of 256 beads. The trend line power law is } \sim 1.07 \text{ without the two lowest grey points. Vertical dashed line superposed from other figure.} \]
The vertical dashed line in figure 6 marks the critical chain length, \( N_C \), which will be got further. The marked \( N_C \) value is necessary to demonstrate two facts. The first, the simulated melt static properties are not influenced by chain length. The second, Rouse time dependence does not show sharp flex near of the \( N_C \) in spite of the curve ends have other slopes. Since this dependence does not permit to find \( N_C \) correctly, this finding will be made further with the help of the scaled dependences [7].

4.3. Scaled dependence of the correlation times on chain length

Ordinate of the scaled dependence is divided by the chain length dependence expected from Rouse model, i.e., \( N^2 \) according to equation (10), as it depicted in figure 7 for three large-scale times, \( \tau_R \), \( \tau_{EE} \), and \( \tau_N \). If the original dependence is coincided with theoretical one, the transformed scaling one would be appeared as horizontal line any deviation from which is very noticeable. The scaling introduce some inconvenience – statistical errors become much better visible due to decreasing of the absolute values along scaled ordinate as it is seen from comparison of figures 6 and 7. Though, this defect is easily circumvented with the help of the analytical trend lines which are duplicated for scaled and original dependence.

Asymptotic trend lines of the low chain length and high chain length branch display clearly the change in the chain dynamic behavior. The low chain length part of curve 1 in figure 7, \( \tau_R/N^2 \), is characterized by large point scattering because short chains do not create coils. In spite of this circumstance this trend line shows power law 2.0, expected for the Rouse regime. The coincidence is probably occasional because the simulated chains have excluded volume, i.e., are not Rouse ones [3, 7]. The long-chain asymptotical branch of this dependence also demonstrates power law 3.0, expected according to equation (9). Intermediate gray points of this and all other dependences are not taken into account for definition of the asymptotical power laws.

Curve 2 in figure 7 for rotational correlation time of the chain end-to-end vector, \( \tau_{EE}/N^2 \), shows asymptotical power laws which are noticeably deviated from ones of equation (10), 1.7 and 2.4. The points scattering of this dependence is much less than that of curve 1, what is defined by the extracting difference for these two correlation times. In spite of the asymptotical power laws difference the intersection of their trend lines for both dependences are at the same chain length value \( N_C = 35 \pm 1 \) within the statistical error. This critical value is marked by vertical dashed line. Thereby, the simulated chains...
of length more than 34÷36 segments or 35÷37 beads behave themselves as entangled ones. In accordance with equation (11) entanglement length has to be in the interval $N_E = (13÷21)$ segments.

Moreover, the lowest dependence in figure 7, the chain orientational correlation time, $\tau_N/N^2$, also displays crossover in the same interval of $N_C$, but with other values of the asymptotical power law, 1.5 and 2.1.

The $N_E$ value is seemed underestimated one in comparison with Monte Carlo simulation data, $\sim 35$ [7-13]. Monte Carlo simulation is traditionally used to investigate dynamical characteristic of various polymer systems due to its much more computational efficiency relative to molecular dynamics simulations. Though, the application of powerful computer during the last years has permitted to use molecular dynamics simulation by many investigators. For example, the similar value of the $N_E \approx 15$ had been obtained in [25]. The dissipative particle dynamics simulation gives even less value, $N_E \approx 13$ [26]. In other words, in spite of the low computational efficiency molecular dynamics simulation permits to study well entangled chains due to less value of the $N_E$ in such simulation.

4.4. Mean-square displacement of the middle and end beads for the different chain lengths

Let’s consider the diffusional behavior the middle bead for various length chains, which permits to find entanglement time $\tau_E$. Figure 8 depicts mean-square displacements of the middle chain segments scaled by short-time regime for $t < \tau_E$, when $g_1(t) \sim t^{0.50}$. This scaling transforms original mean-square displacement into increasing one till $\tau_E$ and into decreasing one after $\tau_E$ according to the equation (5). Furthermore, all curves are collapsed onto a common curve till proper Rouse time of each chain. The collapsed curve maximum defines the entanglement time value, $\tau_E \approx 320$, which was marked in the previous figures.

The sharp lift of each curve is related to the proper Rouse time of each chain. The Rouse chains of 8, 16, and 32 beads in figure 8 have $\tau_R < \tau_E$ and their scaled curves begin to increase before the maximum. The entangled chains of 64, 128, and 256 beads have $\tau_R > \tau_E$ and demonstrate their scaled curves lift much later of $\tau_E$. The dashed line $\sim t^{0.25}$ shows that this regime is clearly visualized only for the longest chain of 256 beads. The curve local minimum of all entangled chains marks transformation of the time regime from $\sim t^{0.25}$ to $\sim t^{0.50}$, and at once to the final regime $\sim t$.

**Figure 8.** Time dependence of the middle bead mean-square displacement scaled to the regime $\sim t^{0.5}$ for different chain lengths. The quantity of the chain beads is indicated in the column in the same order as the curves. The vertical arrow shows the estimation of the entanglement time, $\tau_E$. The dotted line marks power law $-0.25$.

**Figure 9.** Ratio of the mean-square displacement of the end bead and the middle bead as function of time for different chain lengths. The quantity of the chain beads is indicated in the column in the same order as the curves.
Though the scaled curves in figure 8 are described by equation (5) only in short time intervals which does not permit to identify power laws in these intervals, but the number of the curves twists clearly manifest the presence of these four diffusional regimes in accordance with equation (5).

Figure 9 shows the simulation results for the ratio of the mean-square displacement of the end bead and the middle bead, $g_2(t)/g_1(t)$. The ratio starts around 1.0 at early times, exhibits a maximum at intermediate times and tends to 1.0 for large $t$. The ratio maximum should be 2.0 at $t \lesssim \tau_R$, expected for the Rouse chain. For a reptating chain the maximum is still expected at $t \approx \tau_R$, but to be larger than 2.0. For the chain of 64 beads the maximum occurs close to 2.0, i.e., to the value expected from the Rouse model, whereas it is larger for chains of 128 beads, ~2.4, and 256 beads, ~2.9. An increase of the maximum beyond the Rouse limit with growing chain length is predicted theoretically for the reptation and proposed a sensible indicator of reptation dynamics [27]. For a reptating chain the disparity between $g_2$ and $g_1$ has to increase because the motion of the inner bead is strongly confined by the tube at intermediate times, whereas end monomers always take part in tube renewal. The data for $N = 128$ and 256 are indicative of such an enhancement beyond the Rouse limit.

Coincidence of the left-hand side of all maxima indicates the identity of the small-scale translational segmental mobility of any chain length till almost its proper Rouse time when the maximum is achieved. This circumstance is preliminary designation of the segmental orientational dynamics identity independently of the chain length as it was also observed in figure 8.

4.5. Dependence of the reptation characteristics on time and chain length

Figure 10 represents the time dependence of the chain diffusional anisotropy, $a(t)$, for the same chain lengths as in previous two figures. In accordance with equation (24) the anisotropy is the more the less $a(t)$ relative to 2.0 corresponding to isotropic diffusion. It tends to zero for infinitely long chain in the time moment of the tube exit. Hence, the simulated chain could be considered as reptating one if $a(\tau_R) \ll 2$.

$a(t)$ for all chains looks like a minimum which is made deeper and wider with chain length increasing. The minimum depression for Rouse chains, of length 8, 16, and 32, is limited by proper Rouse time, the one for all reptating chains, of length 64, 128, and 256, is continued till $\tau_e$ when a middle segment “collides” with tube walls [2]. Further the minimum is continued with constant depth till proper $\tau_M$ which means the time of the tube leaving and the border of the $a(t)$ definition region. The minimum of two shortest chains, of length 8 and 16, corresponds to isotropic diffusion, it is close to 2.0. The minimum horizontal part of the reptating chains, of length 64, 128, and 256, falls below 0.3 and for the longest chain is equal to 0.03, and its extension is three decimal orders in time.

The long minimum plateau implies that the curvilinear diffusion regime along the tube axis and the lateral diffusion regime are described by the same power law, $g_2(t) \sim g_N(t) \sim \tau^{3.1}$, in the plateau time region as it may be found from figure 5. This process of the tube reorganization due to diffusion of surrounding chains in their own tubes is called constraint release [2, 28] or the tube dilation from its pore constraint does not permit to observe the predicted saturation of $g_2(t)$ due to thermodynamical restriction on reptation [15].

Figure 11 shows the chain length dependence of the entanglement length, $N_E(N)$, and the minimum depth, $a(\tau_A)$, from figure 10. Two vertical dashed lines, $N_E$ and $N_C$, restrict the crossover region from Rouse dynamics to reptation one. Curve 1, $N_E(N)$, below $N_C$ increases approximately as end-to-end distance in accordance with equation (19). In other words, primitive path of the Rouse chain is straight line due to absence of entanglements. Near of the $N_E$ vertical dashed line the primitive path length is sharply increased relative to the chain length and then curve 1 is smoothly saturated till asymptotical value $N_E(N) \approx 14$ segments, which is reached after $N_C$.

It is obviously the value $N_E$ could be uniquely defined with the help of equation (19) for the single system of the well entangled chains by time and ensemble averaging of the primitive path length. I.e.,
we needn’t investigate the chain length dependences to find $N_E$ and its value is agreed very well with the data of figure 7 by statistical equation (11) according to which $N_E = 13\pm 22$. This coincidence demonstrates significance of such abstract notions as “primitive path” and “tube” for description of the entangled chain diffusion. Moreover, this analysis permits to expand the physical meaning of the chain critical length. It is usually interpreted as one which sharply changes chain dynamics due to the life time of inter-chain contacts becomes comparable with the characteristic time of some experimental method. Though, it is needed to keep in mind such the contacts are present for short chains with excluded volume also and influence on their motion.

Such the influence is described by dependence 2 for $a(\tau_A)$ in figure 11. It may be approximated by two power laws with crossover in the region from $N_E \approx 14$ to $N_C \approx 35$ segments. The short chain branch demonstrates that the motional anisotropy is also present and slowly expands for Rouse chains as $\sim N^{-0.30}$. The reptating chain branch is sufficiently faster changed $\sim N^{-1.30}$, but slower than $\sim N^{-2.0}$, expected from equation (26). Nevertheless, the lowest point of the dependence, chain of 255 segments, corresponds to the anisotropy $a(\tau_A) \approx 0.03<<2$ and completely satisfies the basic notion of the reptation theory [1, 2] about negligible lateral chain displacement inside the tube.

Second important conclusion may be made from this dependence. To explain fast increase of the chain life time in permanent surroundings it is unnecessarily to use such the factors as local liquid crystal ordering or specific energetic interaction between chains. The excluded volume and one-dimensionality of the long chain provide the main and alone reason of physical nodes origin in polymer melt. This reason were understandable, if one would have remembered the cage effect in liquid due to which even the vicinity of the small molecules is characterized by finite life time [31].

4.6. NMR transverse relaxation in the simulated polymer melt
It has been demonstrated in the previous sections that the chain dynamics in the simulated melt ranges from Rouse dynamics to reptation one. This demonstration is necessary to reveal the crossover influence on the segmental orientational mobility.
Figure 12 represents the integrated comparison of the different characteristic times as chain length dependences. Only mutual behaviour of all curves may be conclusively converted into NMR transverse relaxation time, the curve $T_2$, in accordance with equations (14)-(16).

![Figure 12](image)

**Figure 12.** Chain length dependence of the different characteristic times: Rouse time, $\tau_R$ (dashed line), time of the anisotropic diffusion, $\tau_A$ (circles); chain, $\tau_N$ (triangles), and segmental, $\tau_1$ (squares), orientational correlation times; NMR transverse relaxation time, $T_2$ (rhombus) for subunits inside the chain of length 127 segments. The value 4.0 near of the right angle is power law defined by the trend line. The vertical dashed lines mark $N_E$ and $N_C$.

It is reasonable to begin from the simplest practically horizontal dependence for the segmental orientational correlation time, $\tau_1$, which defines the most part of the OACF decay in figure 4 and hides information about residual dipole interaction controlling by orientation of the chain as whole. Its behavior is well-known from the multitude of the NMR experiments [3, 30] and indicates independence of the small-scale orientational mobility on chain length.

The highest dashed dependence, $\tau_R$, determines the above mentioned thermodynamical limit for all characteristic large-scale times in the polymer melt [15] and verifies the consistency of simulated data to experiments [3, 30]. The chain end-to-end vector orientational correlation time, $\tau_N$, is partly coincided with Rouse time for short chains, but becomes lower it for reptating chains. The time of anisotropic diffusion, $\tau_A$, is the smallest in the Rouse region, but shows fastest increasing with extraordinary large power law, 4.0. The smallness of the $\tau_A$ relative to even $\tau_1$ and moreover $\tau_N$ means the isotropy of as small-scale as large-scale orientational mobility of the Rouse chains.

The small-scale segmental mobility anisotropy is appeared when $\tau_A$ transcends $\tau_1$ in the region before $N_E$. It means the segmental orientation becomes a few anisotropic, because it partly relaxes during time of anisotropic diffusion. The appeared residual dipole interaction is influenced only by chain orientation as whole with $\tau_N$. The small-scale mobility anisotropy and residual dipole interaction continue to increase till $N_C$ when $\tau_A$ transcends $\tau_N$, later they reach saturation and become constant for reptating chain according to curve 1 in figure 11. Further excess of $\tau_A$ over $\tau_N$ is already unimportant and unobservable in NMR relaxation because $\tau_N$ comes into region of solid-like behavior relative to the constant value of the residual dipole interaction [24].

Exhaustive treatment of the transverse relaxation behavior is outside of this study because it needs great amount of additional simulated data. But qualitative $T_2$ dependence consisted with above discussion can be found for various subunits inside one of the simulated chains of length 255 segments. Such the dependence on subunit length is inaccessible in NMR experiment, but it gives direct information about influence of the increasing small-scale motional anisotropy on $T_2$ according to equations (14) and (16). The curve of effective $T_2$ in figure 12 is got by building of OACF for subunits of length from...
1 to 200 segments in suggestion of the same rigid lattice second moment for all of them. Then free induction decay was got by transformation (16).

The curve $T_2$ for shortest chains shows fast linear decreasing unusual for polymers, because the shortest chains really mimics small molecules with correlation time $\tau_N$ in interval of the complete motional narrowing [24]. Then long before $N_E$ the rate of $T_2$ decreasing is unexplainably changed, at first sight. But in figure 12 the changing is argued by intersection of $\tau_A$ and $\tau_1$ dependences. This intersection generates motional anisotropy transforming the molecule into short Rouse chain. From this chain length transverse relaxation is controlled by two motions, but the most part of the second moment as previously is controlled by segmental orientation, and increasing residual part of the second moment is controlled by $\tau_N$. Due to smallness of the last contribution the $T_2$ begins to decrease very slowly relative to the small molecules. The simplest equation to describe this dependence is different time scale approximation [3] or, so-called, model free theory [34], both of which divide overall OACF into two parts

$$C(t) = (1 - S^2) C_I(t/\tau_1) + S^2 C_N(t/\tau_N).$$

Indices 1 and $N$ corresponds, respectively, to the segment and chain orientation. $S$ is local order parameter which is defined by time and ensemble averaging of the second-degree polynomial, $P_2(t)$, in equation (14). $S$ defines the anisotropy of segmental mobility due to onset of entanglements. In accordance with equation (16) the free induction decay is represented by two multipliers, the first of which is constant due to $\tau_1$ constancy, and the second one is slowly decreased due to $\tau_N$ increasing. In other words, the decreasing rate of the $T_2$ curve is caused by appearance of non-zero $S$ value. Transformation of the $T_2$ curve into horizontal line after $N_C$ is explained by onset of the solid-like for residual dipole interaction defined by $S$, and increasing $\tau_N$ value, which does not satisfy now the condition of narrowing [24].

Another explanation of the total $T_2$ curve behavior is guess of lower system temperature, then the curve shape is fully coincided with experimental one [3] without any additional suggestion. But it needs additional checking simulation at various model temperatures.

5. Conclusion
The purpose of present paper is to compare behaviour of translational, rotational and orientational correlation times of the chain in dense polymer melt over wide region of the chain lengths, from non-entangled to entangled dynamics. It turned out that molecular dynamics simulation permits to observe crossover from non-entangled to entangled dynamics because the degree of the coarse-graining is more in the denser polymer melt, than it is usually observed in Monte Carlo simulations. This circumstance results in less value of the entanglement length, $N_E \approx 14$, in comparison to usual Monte Carlo values, $\sim 35$. In turn, it permitted to simulate well entangled chains with 17 entanglements per longest chain. The well entangled chain demonstrates sufficient diffusional anisotropy as it was predicted by the theory of polymer dynamics [1], but time of this anisotropic diffusion is restricted by thermodynamics reasons [15].

The simulated chain length dependences represent the sufficiently demonstrative system of the data to explain qualitatively the behavior of the nuclear magnetic transverse relaxation time in polymer melts from Rouse till reptation regime.

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