Dynamic Arrest in Polymer Melts:
Competition between Packing and Intramolecular Barriers

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We present molecular dynamics simulations of a simple model for polymer melts with intramolecular barriers. We investigate structural relaxation as a function of the barrier strength. Dynamic correlators can be consistently analyzed within the framework of the Mode Coupling Theory (MCT) of the glass transition. Control parameters are tuned in order to induce a competition between general packing effects and polymer-specific intramolecular barriers as mechanisms for dynamic arrest. This competition yields unusually large values of the so-called MCT exponent parameter and rationalize qualitatively different observations for simple bead-spring and realistic polymers. The systematic study of the effect of intramolecular barriers presented here also establishes a fundamental difference between the nature of the glass transition in polymers and in simple glass-formers.

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Since they do not easily crystallize, polymers are probably the most extensively studied systems in relation with the glass transition phenomenon. Having said this, their macromolecular character, and in particular chain connectivity, must not be forgotten. Its most evident effect is the sublinear increase of the mean squared displacement (Rouse-like) arising after the decaging process, in contrast to the linear regime found in non-polymeric glass-formers. Another particular ingredient of polymers is that, apart from fast librations or methyl group rotations, every motion, as local as it be, involves jumps over carbon-carbon rotational barriers and/or chain conformational changes.

In this work we investigate, by means of molecular dynamics simulations, the decisive role of intramolecular barriers on the glass transition of polymer melts, by systematically tuning barrier strength in a simple bead-spring model. We discuss the obtained results within the framework of the Mode Coupling Theory (MCT) of the glass transition [1]. Initially derived for monoatomic hard-sphere systems, the theory has been further developed for more complex systems, including fully-flexible bead-spring chains as simple models for polymer melts [2]. MCT asymptotic laws have been tested in different polymeric systems. The values of the associated dynamic exponents exhibit significant differences between the limits of fully-flexible bead-spring chains and fully-atomistic polymers [3]. In particular, the so-called exponent parameter takes standard values $\lambda \sim 0.7$ for the former case and values approaching the upper limit $\lambda = 1$ for chemically realistic polymers [4]. While the former $\lambda$-values are characteristic of systems dominated by packing effects, as the archetypal hard-sphere fluid, the limit $\lambda = 1$ arises at higher-order MCT transitions [3]. The latter, or more generally transitions with $\lambda \lesssim 1$, arise in systems with different competing mechanisms for dynamic arrest. These systems include short-ranged attractive colloids [5, 6] (competition between short-range attraction and hard-sphere repulsion) or binary mixtures with strong dynamic asymmetry [7, 8] (bulk-like caging and confinement).

Motivated by these analogies, we argue that values $\lambda \lesssim 1$ for real polymers also arise from the competition between two distinct mechanisms for dynamic arrest: usual packing effects and polymer-specific intramolecular barriers. Such barriers are not present in fully-flexible bead-spring chains, which exhibit standard $\lambda$-values [3]. In order to shed light on this question, we perform a systematic investigation of the interplay between packing and intramolecular barriers. Starting from fully-flexible bead-spring chains, stiffness is introduced by implementing intramolecular bending and torsion terms. The barrier strength is systematically tuned in order to induce competition between the former two mechanisms. We restrict to stiffness for which no orientational order is present, and provide a complete dynamic picture of the isotropic phase as a function of the barrier strength. An extensive test of MCT asymptotic laws is performed. Simulation results are described with consistent sets of MCT exponents. A progressive increase of $\lambda$ is induced by strengthening the competition between packing and intramolecular barriers, confirming the proposed scenario.

We simulate bead-spring chains of $N = 10$ identical monomers of mass $m = 1$. Monomer-monomer interactions are given by a corrected soft-sphere potential: $V(r) = 4\varepsilon ((\sigma/r)^{12} - C_0 + C_2(r/\sigma)^2)$, where $\varepsilon = 1$ and $\sigma = 1$. $V(r)$ is set to zero for $r \geq \sigma$, with $c = 1.15$. The values $C_0 = 7\varepsilon^{-12}$ and $C_2 = 6\varepsilon^{-14}$ guarantee continuity of potential and forces at $r = \sigma$. $V(r)$

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is purely repulsive and has no local minima. Thus, it drives dynamic arrest only through packing effects.

Chain connectivity is introduced through a FENE potential \( \Xi \), with \( V_{\text{FENE}}(r) = -\varepsilon K_F R_0^3 \ln[1 - (R_0 r)^{-2}] \), where \( \varepsilon K_F = 15 \) and \( R_0 = 1.5 \). We implement intramolecular barriers by means of the bending, \( V_B \), and torsion potential, \( V_T \), proposed in Ref. [10] (see discussion there), which are defined for each \( i \)-monomer \((1 \leq i \leq N)\): with \( V_B(\theta_i) = (\varepsilon K_B/2)(\cos \theta_i - \cos \Theta_i)^2 \), and \( V_T(\theta_i, \theta_{i+1}, \phi_i, \phi_{i+1}) = \varepsilon K_T \sin^2 \theta_i \sin^2 \theta_{i+1} \sum_{j=0}^{3} a_{i,j} \cos^j \phi_i, \phi_{i+1} \). Chain stiffness is tuned by varying \( K_B \) and \( K_T \), with 0.5°. The non-ergodicity parameter \( a_0 \) is given respectively in units of \( \varepsilon / k_B \) (with \( k_B \) the Boltzmann constant), \( \sigma(m^2/\varepsilon)^{1/2} \), \( \sigma^{-1} \), and \( \sigma^{-3} \).

We investigate, at fixed \( \rho = 1 \), the \( T \)-dependence of the dynamics for different values of the bending and torsion strength, \( (K_B, K_T) = (0, 0), (15, 0.5), (25, 1), (25, 4), \) and \( (35, 4) \). The case \( (K_B, K_T) = (35, 4) \) is also studied for \( \rho = 0.93 \). The total number of chains is \( N_c = 300 \). Periodic boundary conditions are implemented. Equations of motion are integrated in the velocity Verlet scheme [11]. The system is prepared by placing the chains randomly in the simulation box, with a constraint avoiding monomer core overlap. The initial monomer density is \( \rho = 0.375 \). Equilibration consists of a first run where the box is rescaled periodically by a factor 0.99 < \( f < 1 \) until the target density \( \rho \) is reached, and a second isochoric run at that \( \rho \). Thermalization at the target \( T \) is achieved by periodic velocity rescaling. Once the system is equilibrated, a microcanonical run is performed for production of configurations, from which observables are computed. For each state point, the latter are averaged over typically 40 independent samples.

Orientational ordering (induced by chain stiffness) is discarded for all the analyzed cases by measuring the quantity \( F_2(\Theta) = (3 \cos^2 \Theta - 1)/2 \), where \( \Theta \) is the angle between the end-to-end vectors of two chains, and average is performed over all pairs of distinct chains. In all cases we obtain negligible values \( |F_2(\Theta)| < 10^{-2} \).

We compute density-density correlators, defined as \( F(q, t) = \langle \rho(q, t) \rho(-q, 0) \rangle / \langle \rho(q, 0) \rho(-q, 0) \rangle \) where \( \rho(q, t) = \Sigma_j \exp[iq \cdot r_j(t)] \), the sum extending over the positions \( r_j \) of all the monomers in the system. Density self-correlators are defined as \( F_3(q, t) = \langle N_{N_c}^{-1} \Sigma_j \exp[iq \cdot (r_j(t) - r_0)] \rangle \). Results for the former quantities are shown in Fig. [11] at several \( q \)-values, for two state points with non-zero barriers, at \( T \) close to the critical MCT temperature (see below). As usual, a plateau is observed in the interval corresponding to the caging regime, i.e., the temporary trapping of a particle by its neighbors. This interval is known as the \( \beta \)-regime within the framework of MCT. The second decay, corresponding to full relaxation of density fluctuations of wave vector \( q \), is known as the \( \alpha \)-regime, and is often described by an empirical Kohlrausch-Williams-Watts (KWW) function, \( A_q \exp \{-(t/\tau_q^\beta)\} \), where \( A_q \), the KWW time \( \tau_q^\beta \) and the exponent \( \beta_q \) are \( q \)-dependent.

Next we summarize the basic predictions of MCT and test them in the present system. In its ideal version, MCT predicts a sharp transition from an ergodic liquid to an arrested state (glass) at a given value of the relevant control parameters — here \( x = (T, \rho, K_B, K_T) \). When crossing the transition point \( x = x_c \) the long-time limit of \( F(q, t) \) and \( F_3(q, t) \) jumps from zero to a non-zero value, denoted as the critical non-ergodicity parameter \( \langle f_0^c \rangle \) and \( \langle f_0^c \rangle \), respectively. MCT predicts asymptotic laws for dynamic observables. Such laws are characterized by dynamic exponents that are \( q \)- and state-point independent. They are univocally determined by the static correlations at \( x = x_c \). Moreover, all the dynamic exponents are univocally related to a single one, the exponent parameter \( \lambda \) (see below), which is the basic one controlling all MCT asymptotic laws. Now we summarize the main ones.

For ergodic states close to \( x_c \), the initial part of the \( \alpha \)-process (i.e., the von Schweidler regime) is given by a power law expansion [11]:

\[
F(q, t) \approx f_q^\alpha - h_q(t/\tau_\alpha)^b + h_q^{(2)}(t/\tau_\alpha)^{2b},
\]

and analogously for self-correlators with \( 0 < b \leq 1 \). The non-ergodicity parameters and the prefactors \( h_q^\alpha \) and \( h_q^{(2)} \) only depend on \( q \) and are different for each correlator. The \( \alpha \)-relaxation time \( \tau_\alpha \) only depends on the separation parameter \( |x - x_c| \). MCT predicts a divergence [12] according to the power law \( \tau_\alpha \propto |x - x_c|^{-\gamma} \).

In practice \( \tau_\alpha \) can be defined as the time \( \tau \) where \( F(\xi_{\text{max}}, \tau) \) decays to some small value \( \varepsilon \) far below the plateau, with \( \xi_{\text{max}} \) the \( q \)-value at the maximum of the static structure factor \( S(q) = (N_{N_c})^{-1} \rho(q, 0) \rho(-q, 0) \). Here we will use \( \tau_{0.2} \). The exponent \( \gamma \) is given by [11]:

\[
\gamma = (1/2a) + (1/2b).
\]

As mentioned above, the full \( \alpha \)-decay can be described by a KWW function. In the limit of large \( q \) MCT predicts [13] for the KWW times a power law \( \tau_q^\beta \propto q^{-1/b} \). The exponents \( a, b, \) and \( \gamma \) are univocally related to the exponent parameter \( \lambda \leq 1 \) through [11]:

\[
\lambda = \frac{\Gamma^2(1 + b)}{\Gamma(1 + 2b)} = \frac{\Gamma^2(1 - a)}{\Gamma(1 - 2a)}.
\]
investigated, with different strength of the intramolecular barriers. Figs. 1-3 display some representative examples. Fig. 1 shows at fixed density \( \rho = 1 \) for different barrier strength. Lines in (b) and (c) are fits to Eq. (1). A good description is obtained with the same non-ergodicity parameters. The fully flexible case \((B_B = 4, K_T = 0)\), which also shows a test of the predictions (see text for notations) for different barrier strength. Lines in (b) and (c) are fits to respectively \( \alpha \propto q^{-1/b} \) and \( \propto (T-T_c)^{-\gamma} \) (see text).

With \( \Gamma \) the Euler’s Gamma function.

When numerical solutions of the MCT equations are not available, the former non-ergodicity parameters, prefactors and exponents are obtained as fit parameters from simulation or experimental data. Consistency of the analysis requires that dynamic correlators and relaxation times are described by a common set of exponents, univoquely related through Eqs. (2,3). This consistent test has been done for all the systems here investigated, with different strength of the intramolecular barriers.
It also includes the mean chain end-to-end radius at $T_c$ and barrier strength. Also included are the mean chain end-to-end radius $R_{ee}$ at $T_c$. 

**Table I:** Values of the MCT exponents and critical temperature $T_c$ for different $\rho$ and barri strength. This demonstrates the consistency of the data analysis. For comparison, Fig. 3 also includes results for the fully flexible systems. The sharp transition and time divergence are prevented within a broad region $K_B = K_T = 0$. 

Table 3 displays the results of the MCT analysis (dynamic exponents and $T_c$) for all the investigated cases. It also includes the mean chain end-to-end radius at $T_c$, $R_{ee}$, as computed from the simulations. $R_{ee}$ provides a qualitative characterization of chain stiffness. From numerical values in Table 3, a clear correlation between the exponent parameter $\alpha$ and chain stiffness is unambiguously demonstrated. The competition between packing effects and intramolecular barriers induces a progressive increase of $\lambda$ from the value $\lambda = 0.76$ for fully-flexible chains to $\lambda = 0.89$ for the stiffest investigated chains. 

This observation rationalizes the difference observed between MCT exponents for fully-flexible bead-spring chains and chemically realistic polymers. Table 3 shows a representative compilation of exponents for glass-formers of very different nature. Exponents for fully-flexible bead-spring chains are similar to those of non-polymeric glass-formers, including the hard-sphere fluid, i.e., the archetype glass-former dominated by packing effects. Chemically realistic polymers of increasing complexity exhibit instead values approaching the limit $\lambda = 1$ characteristic of higher-order MCT transitions. The systematic study presented in this work strongly suggests a competition between general packing effects and polymer-specific intramolecular barriers as the origin of this difference. It also suggests a fundamental difference in the nature of the glass transition in real polymers — driven by the former competing mechanisms — as compared to simple glass-formers. 

**Table II:** MCT exponents for different glass-formers. Data are taken from [1] and references therein. UA and FA denote respectively coarse-grained united atom and fully-atomistic models. 

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12. Actually, deviations from this power law are generally observed for sufficiently small values of $|\kappa - \infty|$. The sharp transition and time divergence are prevented by ergodicity-restoring hopping events not included in ideal MCT. Still, MCT predictions are usually fulfilled within a broad $x$-window. 
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14. Confirmation of an underlying higher-order transition ($\lambda = 1$) would require solving the MCT equations. Work on this question is in progress. Having said this, the trend displayed by data of Table 3 suggests that the former would be located at regions of stronger barriers or lower $\rho$. There, the isotropic phase becomes unstable. This prevents the observation of values $\lambda \rightarrow 1^−$.